



Clinker Burning Kinetics and Mechanism

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TECHNICAL UNIVERSITY OF DENMARK (DTU)

Clinker Burning Kinetics and Mechanism

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Ph.D. Thesis

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Preface

The present dissertation summarizes the research activities between March 2008 and August 2011 performed as a member of the Combustion and Harmful Emission Control (CHEC) research center at The Department of Chemical and Biochemical Engineering at the Technical University of Denmark (DTU) and is submitted as a partial fulfillment for obtaining the Ph.D. degree at the DTU. The dissertation was supervised by Kim Dam-Johansen (DTU), Flemming Frandsen (DTU), Stig Wedel (DTU) and Kirsten Theisen (FLSmidth A/S). Experimental was mainly carried out at DTU and at the FLSmidth laboratories in Dania (Denmark). Financial support was granted by The Danish National Advanced Technology Foundation and FLSmidth A/S.

I would like to thank my supervisors Kim Dam-Johansen, Kirsten Theisen, Flemming Frandsen and Stig Wedel for their guidance and support during the study. Discussions have been always interesting and challenging, catalyzing my professional and personal development immensely.

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I owe many thanks to all the staff at the FLSmidth laboratories in Dania for providing me with help in the XRD, XRF, Free lime- and Light microscopy- analysis. The vast amount of sample analyses wouldn't have been possible without their help.

M.Sc. and B.Sc. students Anette Münther and Ingeborg Jørgensen are gratefully acknowledged for their contribution to the project. A special thanks to M.Sc. Lars Jørgensen for his great effort and patience to test the maiden setup, especially in extracting results. May he never need to grind any clinker again.

At last, many thanks to my family for all their support through the last 4 years. Big thanks to Matthias, who has been there, when times were tough.

Kgs. Lyngby, January 31st, 2012

Summary

The industrial cement process is subject to several changes in order to reduce the high energy consumption and thereby increase the profitability of cement production. These changes also affect the core of the entire cement producing process: the clinker formation in the rotary kiln. Thus, in order to maintain or even improve clinker quality (and output), we need a better understanding of the development of clinker properties inside the kiln to react upon the impact of process changes.

Clinker formation in industrial rotary kilns is very complex due to a vast number of interacting parameters: kiln dimensions, rotation velocity, temperature, gas composition, heat transfer phenomena, etc. These conditions can only be partly simulated in ordinary lab-scale experiments. Thus, the objectives of this project have been to establish test equipment to simulate the industrial clinker burning process on a laboratory scale and to conduct clinker formation experiments in order to derive knowledge on gradual clinker property development, as a function of different process parameters.

A new lab-scale setup rotary kiln simulator (RKS) was designed and built for this purpose. It is assembled of two parts: an ordinary lab-scale heating furnace and a sample motion system. The motion system consists of a SiC tube, which moves the sample, placed in a Pt/Rh-crucible, at a chosen velocity through the heating furnace. Simultaneously, the sample is rotated around its horizontal axis with a chosen rotation velocity. The heating furnace consists of five individual heating zones, which are set to obtain a temperature ramp from ~ 900 - 1540 °C. Furthermore, the atmosphere in the system can be set to any mixture of N_2 , O_2 and CO_2 . Thus, the rotary kiln simulator features most important parameters of the industrial cement rotary kiln (ICRK): gradual temperature increase, rotation velocity and gas phase composition.

An investigation of clinker formation vs. heating profile and rotational velocity were conducted, and the influence on the clinker phase composition and clinker agglomeration was deduced. Independent of the raw meal used, the different clinker phases were formed in three stages: 1. C_2S , C_3A and C_4AF formation at ~ 900 - 1350 °C; 2. Clinker melt formation at ~ 1350 - 1400 °C; and 3. C_3S formation at >1350 °C. The first temperature of clinker melt occurrence varied slightly depending on the type of raw meal used.

The influence of different heating profiles on clinker formation was studied, and it was observed that C_3S formation was more complete, the faster the sample was heated to a temperature $>1400\text{ }^{\circ}\text{C}$. However, only with relative long residence times above this temperature clinker phase compositions similar to industrial clinker, i.e. with high C_3S concentration and low CaO concentration, were obtained. It was concluded, that the maximum temperature of $1540\text{ }^{\circ}\text{C}$ in the RKS does not simulate the maximum temperature in the ICRK. Thus, the maximum temperature of $1450\text{ }^{\circ}\text{C}$, as is often stated in literature, is likely often not applicable.

Agglomeration of the raw meal was observed to start already at $900\text{ }^{\circ}\text{C}$. The agglomerates formed are first rather weak, but increase in hardness with increasing temperature. The size of the agglomerates as well as the amount formed was found to be dependent on the rotation velocity: the higher the rotation velocity, the higher was the amount of agglomerates $< 1\text{ mm}$. The higher rotation velocity also resulted in a decrease of the total amount of agglomerates, whereas the amount of material lining on the reactor walls increased.

The establishment of the RKS setup will allow more realistic clinker formation studies in future and thus potentially an experimental lab-scale access to the understanding of important parameters in the ICRK. The obtained qualitative and quantitative data on clinker phase composition and on agglomerate formation depended on operational parameters are essential for the development/improvement of models for bed material process in the ICRK, and for the development steps to improve the reactor technology.

Dansk resumé:

Cementproduktion i industriel skala har gennem årene undergået flere betydelige ændringer med henblik på at nedbringe energiforbruget og dermed øge rentabiliteten af processen. Disse ændringer har naturligvis også påvirket klinkerdannelsen i rotérovnen. Med henblik på at forbedre eller opretholde klinkerkvalitet (og -kvantitet), har cementproducenterne derfor brug for bedre forståelse af udviklingen af klinker karakteristika og -egenskaber i rotérovnen.

Klinkerdannelse i industrielle cement rotérovne er en kompleks proces der er influeret af et utal af interagerende parametre: ovndimension (længde + diameter), rotationshastighed, temperaturprofil igennem ovnen, gassammensætning i ovnen, varmetransportfænomener, osv. Disse forhold har det hidtil kun i yderst begrænset omfang været muligt at simulere i lab-skala eksperimenter. Derfor har det primære formål med dette projekt været at etablere lab-skala testudstyr der kan simulere den industrielle cementklinkerbrændingsproces, samt anvendes til at studere klinkerdannelse med henblik på at udlede viden om dynamikken i klinkerdannelsesprocesserne, som funktion af forskellige drifts- og procesparametre.

Et nyt lab-skala set-up, en rotérovnssimulator (RKS), er blevet designet og bygget til dette specifikke formål. Den består af to dele: en høj-temperatur ovn, og et set-up som kan bevæge og rotere prøven. Sidstnævnte består af et SiC rør der anvendes til at bevæge prøven med en given hastighed gennem høj-temperatur ovnen og samtidigt rotere prøven omkring dens vandrette rotationsakse med en foruddefineret rotationshastighed. Prøven er placeret i en Pt / Rh-smeltedigel for enden af SiC røret. Høj-temperatur ovnen har fem individuelle opvarmningszoner, der er indstillet således at temperaturen øges fra ~ 900 til ~ 1540 ° C med en given temperaturprofil. Atmosfæren i systemet består af enhver blanding af N₂, O₂ og CO₂. Rotérovnssimulatoren kan derfor simulere alle de vigtige driftsparametre der karakteriserer den industrielle cement rotérovn (ICRK): gradvis temperaturstigning, rotationshastighed, gasfasens sammensætning og råmaterialets sammensætning.

En detaljeret undersøgelse af klinkerdannelse som funktion af opvarmningsprofil og rotationshastighed er blevet gennemført i dette projekt, og indflydelsen af disse parametre på klinkerfasens sammensætning og agglomerering af klinker er blevet beskrevet. Uafhængigt af det anvendte råmel, blev de forskellige klinkerfaser dannet i tre trin: Først C₂S, C₃A og C₄AF-dannelse i temperaturintervallet ~ 900 - 1350 ° C, derefter klinker smeltedannelse i intervallet ~ 1350 - 1400 ° C, og endelig C₃S-dannelse ved temperaturer over 1350 ° C. Den første

klinkersmeltetemperatur varierede kun minimalt som funktion af sammensætningen af det anvendte råmel.

Indflydelsen af temperatur-profiler, f.eks. jævn temperaturstigning eller trinvis ændring i temperaturen, på klinker dannelsen er også blevet undersøgt, og det blev konstateret at C3S-dannelsen var mere fuldstændig, jo hurtigere prøven blev opvarmet til en temperatur højere end 1400 ° C. Dog var en relativ lang opholdstid ved temperaturer højere end 1400 °C nødvendigt for at klinkerne fik en fasesammensætning, der svarer til industrielle klinker, hvor koncentrationen af C3S er høj og CaO koncentrationen lav. Det blev konkluderet, at den maksimale temperatur på 1540 ° C i RKS, ikke simulerer den maksimale temperatur i en industriel rotérovn.

Det blev i det eksperimentelle arbejde konstateret at agglomerering af råmaterialet starter allerede ved 900 ° C. De dannede agglomerater er indledningsvist relativt svage, men opnår øget hårdhed med stigende temperatur. Størrelsen af agglomeraterne samt den mængde i hvilken de dannes, er afhængig af rotationshastigheden: Jo højere rotationshastighed, jo større mængde agglomerater <1mm. En højere rotationshastighed resulterede også i et fald i den samlede mængde agglomerat, mens mængden af materialeforing på reaktorvæggene steg.

Etableringen af en lab-skala rotérovnssimulator vil også i fremtiden give mulighed for at lave mere realistiske undersøgelser af klinkerdannelse i fremtiden, og dermed potentielt en eksperimentel adgang til forståelsen af vigtige parametre i ICRK. De opnåede kvalitative og kvantitative data for klinkerfasesammensætning og agglomeratdannelse er afgørende for udvikling / forbedring af modeller for interaktioner mellem materialerne i partikellejet i ICRK, og for udviklingen af en forbedret reaktortechnologi til anvendelse i cementproduktion.

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Chapter 1

Introduction

1.1 Background

Cement is the key material in building and construction industry, noticeable by the rapidly increasing world production. Simultaneously, the cement producing industry is obligated to constantly modernize and improve the process technology to meet on the one hand the increasing governmental constraints on environmental impact and to increase the profitability by increasing the production capacity and reducing the energy consumption. Over the last few decades, cement rotary kiln technology has been steadily improved: the incremental shift from the wet- to the dry-production process, the separation of the location of different chemical reactions (raw meal calcination $\leftrightarrow$ clinkerization), gas bypass systems, energy recovery systems and state-of-the-art emission control systems are some of the changes that have increased production capacity greatly and reduced energy consumption and pollution. Nonetheless, the cement production remains a highly energy consuming and polluting sector in the industrial world. Special focus has been laid on the high energy consumption (thermal and electrical energy) involved in cement production, since fuel costs amount significantly to the manufacturing costs. One possibility to reduce the fuel costs is to introduce alternative fuels, such as household waste, biomass, plastics, rubber, tires, paper waste, sewage sludge, waste oil and solvents, into cement production.¹⁻⁶ As an example, Cemex UK replaced 52 % of traditional fossil fuels with alternative fuels (accounting to more than 300,000 tonnes of waste) in two cement works in Great Britain in 2010 and aims for further increases over the coming years.⁷ Other possibilities to reduce the thermal energy consumption might involve radical changes with respect to in the clinker burning technology (e.g. change of reactor type⁸) and/or final clinker composition (e.g. belite-based clinkers), since modern process technology is already optimized to a large extent in order to minimize energy losses; applied thermal energy is already close to the minimum energy predefined by reaction chemistry. Electrical energy is consumed by raw meal pre- and clinker/cement post-treatment processes such as material grinding. A reduction in energy consumption is mainly possible by changing the clinker properties to improve its ‘grindability’. Raw material grinding can only be optimized to a limited extent, due to the nature of the different utilized raw materials.

Whatever changes are conducted, they affect directly or indirectly the heart of the cement production: the clinker formation in the cement rotary kiln. For example ash residues of alternative fuels differ from conventional fuels, and many contain for example also calcite, sand and/or glass (among others). These materials, introduced at different ends into the rotary kiln (either from the calciner or from kiln the burner), react with the solid bed material. In general, to be able to react upon such important effects on clinker formation, the processes in the rotary kiln need to be understood.

1.2 Objectives of the Project and Structure of the Thesis

The objectives of this Ph.D. study have been to establish background knowledge on correlations of process conditions with respect to the development of clinker properties in a cement rotary kiln.

The research on clinker formation can be dated back to the end of the 19th century, and substantial progress has been made in understanding the variety of individual clinker phase formations. Laboratory data have been compared with the experiences of cement plant operations. It is therefore possible to predict approximately the properties of clinker and cement obtained at the end of the process, dependent on starting conditions such as raw meal composition, type of fuel and air/gas mixtures and kiln dimensions. Chapter 2 presents a literature overview with focus on the formation reactions of the various clinker phases as studied in ordinary lab-scale experiments. The results from laboratory-scale studies are discussed with respect to chemical processes occurring in an industrial rotary kiln reactor.

Knowledge on how clinker formation and industrial clinker properties develop dynamically inside the industrial rotary kiln is rare. But, qualitative and quantitative data on the interaction of all process parameters influencing clinker formation in the industrial rotary kiln are essential for further improvement of the rotary kiln (e.g. faster/lower rotation) and/or changes of the reactor for clinker formation (e.g. dividing the rotary kiln in different reactor systems). However, on-site investigations are difficult, since the precise control of the investigated parameters (e.g. gas composition and raw meal composition) is impossible and experimental techniques to measure e.g. the gas and bed temperature inside the kiln are not routinely established. Furthermore, systematic investigations would interrupt the cement production and therefore cause significant additional costs. Thus, the focus has been to establish test equipment, which enables the investigation of clinker formation as it occurs in the industrial cement rotary kiln on a laboratory scale. In Chapter 3

the design and construction of a new lab-scale rotary kiln is described, which was used for clinker formation simulations of the industrial process. Chapter 4 deals with the detailed characterization of the new setup with respect to reproducibility and repeatability of the clinker phase formation.

The aim of the Ph.D.-project has been to study the dynamically development of clinker composition and the physical shape of clinker with the new test equipment and relate the results to the industrial process. Chapter 6 presents clinker formation at experimental conditions comparable to the industrial process, i.e. investigating the influence of e.g. temperature profiles and rotation velocity on clinker phase composition and clinker agglomerate size, respectively. Finally, conclusions and suggestions for further investigations are given in Chapter 7.

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Chapter 2

Literature Review

2.1 Introduction

“Higher! Faster! Further!” – is not just the motto of the Olympic Games; it is a theme, describing progress during the twentieth and twenty-first centuries. The construction world especially has committed itself to the first: Higher! The heights of buildings particularly, always a symbol of power, economical potential and wealth, have increased drastically over the last 100 years (Fig. 2-1).

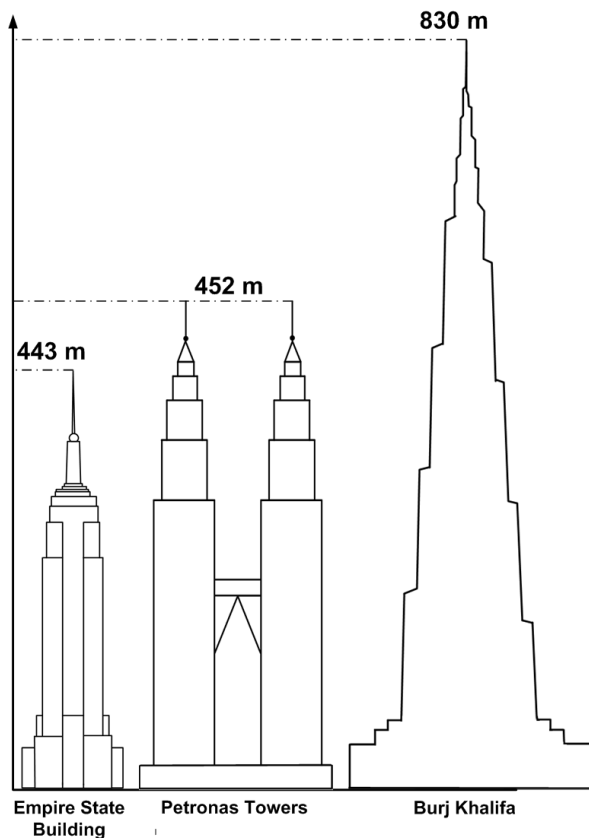


Fig. 2-1: A non-true to scale comparison of buildings: on the left the Empire State Building (USA), the Petronas Towers (Malaysia) in the middle and the Burj Khalifa (UAE) on the right.

One factor among others, which makes high constructions possible, is reinforced concrete. Around 47,000 m³ of concrete was needed for the construction of the Empire

State building (USA).¹ The construction of the Petronas Towers (Malaysia) required approximately 160,000 m³ of concrete,² while the Burj Khalifa (UAE), the tallest building of the world to date, was constructed using circa 330,000 m³ of concrete.³ These numbers symbolize the importance of concrete and it is not surprising, that the production of its key compound, cement, is not only one of the oldest, but also one of the biggest industrial sectors and is still growing. World production increased by a factor 10 between 1950 and 2006. Within only 5 years (2001-2006), the production rose by 35%.⁴ In 2006, a total of 2.54 billion tonnes of cement was produced worldwide, with 47.4% in China, 10.5% in the European Union, 6.2% in India and 3.9% in the US (Fig. 2-2).⁴ This ongoing success is accompanied by constantly changing and improving production technology to meet demand for the cement quality and quantity, fuel efficiency, pollution limitations (emission control) and, last but not least, production profitability. At the heart of cement production are high temperature processes (up to 2000 °C gas temperatures), where raw materials undergo several chemical changes to form clinker crystal phases as the main constituents of most cement types.⁵⁻⁴¹ The reactor (cement kiln), in which these processes occur, has been subject to changes over the last few decades. Whereas the first kilns were bottle shaped batch reactors with limited production capacity,⁴² clinker is nowadays produced mainly in continuously operating rotary kilns with a capacity of 3000-5000 tonnes of clinker per day, or even up to 10,000 tonnes per day in some Asian plants.⁴

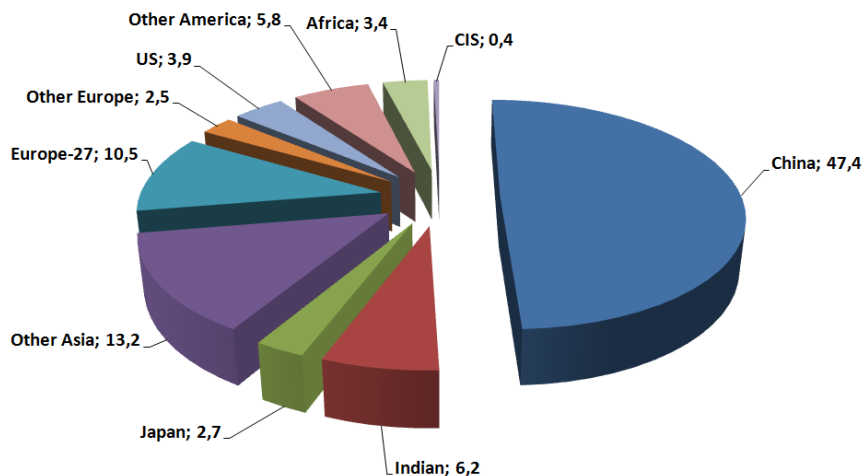


Fig. 2-2: An overview of cement production worldwide in 2006.⁴

The energy required for cement production is provided by the combustion of different kinds of fossil fuels, biomass fuel and waste. The demand for thermal energy equals ~3000-4000 MJ/tonne of clinker for the widely-used dry process (including cyclone pre-heater and calciner).⁴ Additionally, around 324-540 MJ/tonne cement of electrical energy is required for processes such as grinding (raw materials and cement) and exhaust fans.⁹ The main air-pollutant substances related to cement production are, among others, CO₂, CO, nitrogen compounds (e.g. NO_x) and sulfur compounds (e.g. SO₂). About 900-1000 kg CO₂ per tonne of clinker (grey cement clinker) is released, of which 60 % is related to calcination of CaCO₃, while the rest accounts for fuel combustion.⁴ NO_x emissions (mainly NO and NO₂) amount to ~0.3-4.7 kg/tonne of clinker. The main sources for NO_x formation are the combustion of fuel and the reaction of nitrogen in combustion air with oxygen at high kiln temperatures.⁴ Sulfur is brought into the process by raw materials and fuel, and is mostly combined with CaO and alkalis as CaSO₄ and alkali-sulfates in the clinker product and dust. Organic sulfur and sulfidic sulfur is emitted as SO₂ via exhaust gas. The emission depends on utilized raw materials and fuels and differs from one cement works to the other.⁴

Systematic changes and improvements of the cement production process require detailed knowledge about the clinker formation process itself. The research in that topic can be dated back to the end of the nineteenth century, and substantial progress has been made in understanding the variety of individual clinker phase formations. Due to the difficulty and high costs of investigating reactions and reaction conditions directly in an industrial reactor, research has been mostly carried out in the laboratory.¹⁰⁻³⁷ Several books^{7,38-40} and some review papers^{9,41} have summarized clinker formation reactions. Laboratory data have been compared with the experiences of cement plant operations. Therefore, it is in general possible today to predict the properties of clinker and cement obtained at the end of the process, dependent on starting conditions such as raw meal composition, type of fuel and air/gas mixtures (determining the temperature profile in the kiln) and kiln dimensions (determining the retention time of the solid material). But, only a few

attempts, to the author's knowledge, have been made to present the reaction mechanisms of clinker phase formations as they emerge in the industrial process.⁹

In this literature review, the vast amount of research on clinker phase formation at temperatures between 900 and 1500 °C is evaluated and summarized. It provides a detailed description of the formation of the silicate, aluminate and ferrite phases from the four major compounds CaO, SiO₂, Al₂O₃ and Fe₂O₃ of typical cement raw meals. Results from laboratory-scale studies are discussed with respect to chemical processes occurring in an industrial rotary kiln reactor.

The influence of minor and trace compounds on clinker formation/clinker quality will not be addressed in this article, unless stated differently, as this topic has already been intensively reviewed elsewhere.^{38,39}

2.2 Portland Cement Production

Cement is a hydraulic binder forming a paste with water, which sets and hardens due to hydration reactions⁵. It creates the strength, durability and soundness of concrete and mortar. Cement is either classified by its composition or in respect to its performance-related properties by national or international institutions. However, the most common classifications are related to the European Standards for Common Cements (e.g. EN 197-1) defined by the European Committee for Standardization⁴³ and the ASTM Standards (e.g. C150/C150M and C595/595M) defined by the American Society for Testing and Material⁴⁴. A detailed overview of the different cement classifications is given in ref. ⁵.

Up to now Portland cements are the most produced cements yearly. The main constituent of these cements is clinker (often termed as Portland cement clinker), which itself is composed of 40-80 wt.% C₃S, 10-50 wt.% C₂S, 0-15 wt.% C₃A and 0-20 wt.% C₄AF.⁴

Therefore, the following description of industrial process is based on the Portland cement production.

2.2.1 Portland Cement Clinker

Clinker, as the main constituent of cement, is composed of various crystal phases, the following of which are the most important: alite, belite, aluminate and ferrite. Alite and

belite are calcium silicate phases. Consisting only of CaO and SiO₂, alite is a tricalcium silicate phase (Ca₃SiO₅) and belite a dicalcium silicate phase (Ca₂SiO₄). The aluminate phase, formed by pure CaO and pure Al₂O₃, is a tricalcium aluminate phase (Ca₃Al₂O₆) and the ferrite phase, formed by pure CaO, Al₂O₃ and Fe₂O₃, is a tetracalcium aluminoferrite phase (Ca₄Al₂Fe₂O₁₀). It is common to abbreviate the chemical formulae as follows (Tab. 2-1):

Tab. 2-1: Abbreviation of the chemical formulae used in the cement field.⁷

Chemical compound	Abbreviation	Clinker phase	Clinker phase Abbreviation
CaO	C	Ca ₃ SiO ₅	C ₃ S
SiO ₂	S	Ca ₂ SiO ₄	C ₂ S
Al ₂ O ₃	A	Ca ₃ Al ₂ O ₆	C ₃ A
Fe ₂ O ₃	F	Ca ₄ Al ₂ Fe ₂ O ₁₀	C ₄ AF
		Ca ₁₂ Al ₇ O ₃₃	C ₁₂ A ₇

Pure oxides are only available for laboratory investigations of clinker formation. In the industrial process the raw material contains various impurities,^{5,7} which form clinker phases incorporating impurities or forming solid solutions with minor compounds. Therefore, it is more appropriate to use the phase names “alite”, “belite” -and so on-, since these express the clinker phases including impurities.

2.2.2 Charge Materials

The main constituents of the raw materials required for cement production are calcium oxide (CaO), silicon dioxide (SiO₂), aluminum oxide (Al₂O₃) and iron oxide (Fe₂O₃).⁴⁵ Typical sources of these oxides are limestone, chalk, marl, clays (kaolinite, illite, feldspar) or shale, tuff, oil shale, bauxite and iron ore.^{39,45} These materials often contain alkalis, earth alkalis, heavy metals, sulfate, sulphide, phosphate, fluoride and chloride compositions in lower concentrations.^{7,39,45,46} Besides natural materials, waste products from other industrial processes, such as lime sludge or fly ash from coal combustion, can be added. The addition of relatively pure limestone, sand or iron ore might be necessary

to adjust for absent chemical compounds and achieve the standards required for cement.^{5,45} A typical chemical composition of four-component raw meal is listed in Tab. 2-2.⁵ The chemical composition of the raw materials is constantly controlled in plant laboratories.

Tab. 2-2 Typical chemical composition of a four component raw meal.⁵

	Limestone (wt.%)	Shale (wt.%)	Sand (wt.%)	Iron Oxide (wt.%)	Kiln feed** composition (wt.%)
Dry material used	73	22.5	4.2	0.3	-
SiO ₂	1.4	37.9	95.0	2.7	20.1
Al ₂ O ₃	0.5	16.5	1.4	6.6	6.3
Fe ₂ O ₃	0.2	5.1	1.3	84.0	2.4
CaO	53.7	15.4	1.0	2.7	64.4
CaCO ₃	95.9	27.5	-		-
Minor* compounds	2.0	13	2.3	6.7	6.8

* Modification of the original.

** Decarbonized material.

Several stages of cement production occur at elevated or high temperatures such as the drying of raw materials, the endothermic decarbonisation reaction of limestone and clinker formation reactions at up to 1500 °C. The heat required is provided by the combustion of fuel, namely black coal, lignite, heavy and light fuel oil, fuel gas and/or petroleum coke (Tab. 2-3). These traditional fuels are nowadays increasingly substituted by alternative fuels such as scrap tires, waste oil, fuller's earth, wood waste, plastic waste and fractionized commercial and domestic waste,⁴⁷⁻⁶⁰ thus disposing waste and reducing the depletion of natural resources. Non-combustible fractions of alternative fuels are utilized for the clinkerization as for example the steel carcasses of tires are a significant source of iron oxide. Thus, alternative fuels are completely salvaged.⁴⁵

Tab. 2-3: Fuel types and consumption at cement plants in the European Union in 2006.⁴

Fuel type	Consumption (%)
Petcoke (fossil)	38.6
Coal (fossil)	18.7
Petcoke and coal (together)	15.9
Fuel oil	3.1
Lignite and other solid fuels	4.8
Natural gas	1.0
Waste fuel	17.9

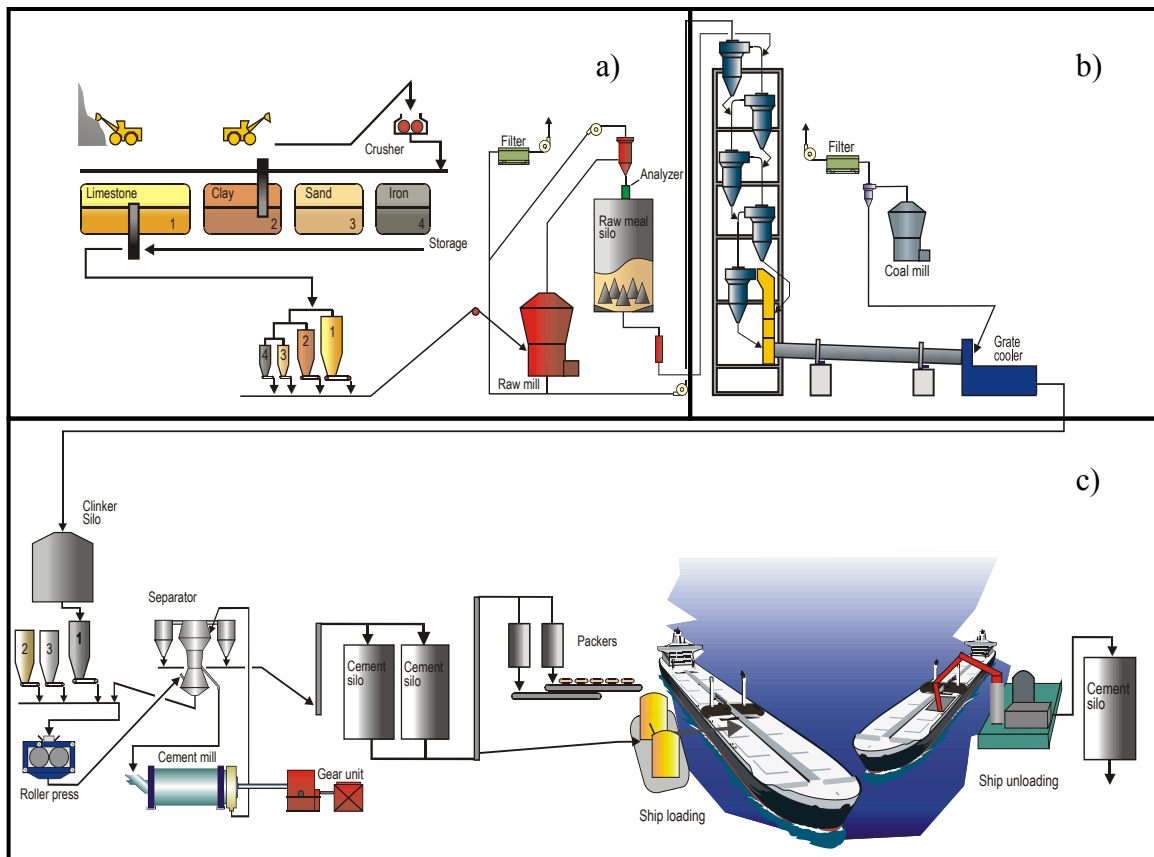


Fig. 2-3: Overview of a cement production plant. a) Pre-treatment of the raw materials; b) High temperature process; c) Post-treatment of clinker/cement.⁶¹

2.2.3 Raw Meal Pre-treatment

Mined raw materials are crushed and, depending on fluctuations in the chemical composition, separately pre-homogenized to provide constancy of cement product quality (Fig. 2-3a). Further raw meal preparation was originally distinguished mainly into dry- and wet pre-treatment, depending on the moisture content of the raw materials.^{5,39,45} A feedstock with a moisture content of >15 wt.% was often prepared under wet conditions,⁵ where water was added in order to achieve a slurry with a water content of 25-50 wt.%.^{5,39} The advantage of this method is the achievement of high raw meal uniformity. However, the application of the wet method decreased over the years since the removal of the water is energy-intensive and, due to fuel prices, expensive. If a wet preparation cannot be avoided, parts of the water are removed by filtration, decreasing the water content to ca. 20 wt.%.⁵

The more cost-efficient dry pre-treatment method is by far the most employed process in cement production, which is why the following process descriptions focus only on the dry method-based cement plants. There, raw materials are often ground and dried simultaneously. The blending of the different materials, including secondary raw material to obtain clinker raw meal, is carried out either by simultaneous grinding or after the grinding step by air agitation in large silos.^{5,45} Thereby, comparable homogeneities with respect to the wet method are achieved.^{5,45}

2.2.4 Pre-heating

Clinker raw meal is heated in the cyclone pre-heater (Fig. 2-3b, Fig. 2-4a). The pre-heater is basically a series of cyclones arranged in 50-120 m high towers. Hot gases (1000 °C) from the calciner and rotary kiln heat the raw meal in counter-current flow, increasing the feed temperature from 200 °C to 800 °C in less than a minute.^{7,39}

High contents of inorganic volatiles in the gases, mostly sodium and potassium sulfates and chlorides, are problematic, when released from the raw material or fuel in the rotary kiln,⁶² as they may condense at the pre-heater walls forming solid deposits, which limits the motion of gas and material.⁷

2.2.5 Calcination

The separation of the calcination process of calcareous materials from processes in the rotary kiln improved the cement production significantly (Fig. 2-4 b).^{63,64} The rotary kiln decreased in size or, with unchanged kiln dimensions, production capacity increased, thus decreasing investment and operational costs.^{7,45}

The hot raw meal enters the calciner at about 800 °C from the preheater. The energy required for the endothermic decarbonisation reaction (calcination) is obtained from hot rotary kiln gases and additional combustion of fuel. Most often, hot air from the clinker cooler, so-called tertiary air, is utilized as combustion air (Fig. 2-4f). The consumption of fuel for calcination can account for up to 60% of fuel needed for cement production.⁴⁵ The degree of decarbonisation constitutes 90-95% and solid material enters the rotary kiln with a temperature of about 900 °C.^{7,45}

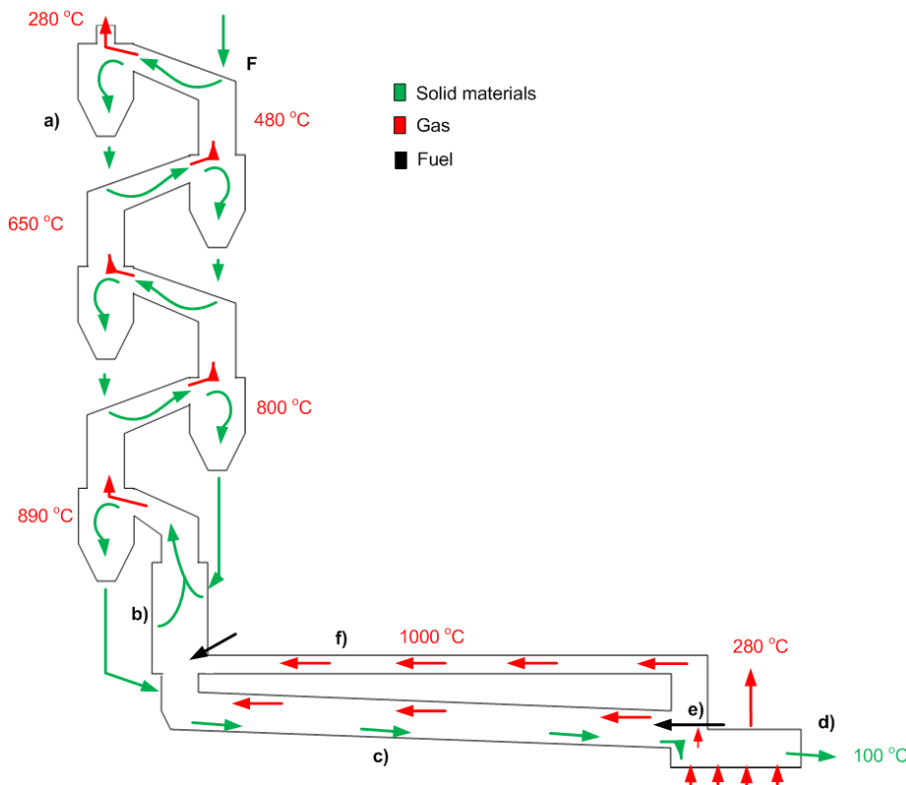


Fig. 2-4: An In-line calciner pre-heater system. a) the pre-heater tower, b) the pre-calciner, c) the rotary kiln, d) the clinker cooler, e) burner and secondary air inlet, f) tertiary air pass.⁶³

2.2.6 Clinkerization

Rotary kilns vary greatly in length and diameter depending on the design of the whole pyro-process kiln system (includes all from raw meal pre-heating till clinker cooling). Typical dimensions for rotary kiln systems with cyclone pre-heater and calciner are 50-100 m in length and 3-7 m in diameter (length to internal diameter ratio ~11-16).^{64,65} These kilns operate typically at a tilt of 1-3° from horizontal and with a rotation velocity of 2-4.5 rev/min (Fig. 2-4c), which results in material retention times in the kiln of circa 20-40 min.⁶⁴ The pre-calcined solid meal is fed into the kiln at the higher end, solid or liquid fuel along with primary air is blown into the kiln and combusted at the lower end of the kiln,⁷ creating a flame with temperatures of around 2000 °C.⁶⁶ Additionally, secondary air from the clinker cooler is also drawn into the kiln for fuel combustion (Fig. 2-4e).⁷ The calcined meal moves counter current to the hot gases toward the hot region (sintering zone) of the kiln, thereby, achieving heat transfer between gases, solids and the kiln walls. The calcined feed is heated up to ~1500 °C, leading to several chemical reactions and mineralogical changes in the different zones of the kiln: decomposition of the remaining uncalcined CaCO_3 and, formation of the clinker phases. At temperatures up to 1250 °C solid state reactions occur, and the belite, aluminate and ferrite phases are gradually formed. In addition, at these temperatures inorganic volatiles are released from the feed material and fuel consisting mainly of alkalis, sulfates and chlorides, which condense and form deposits as rings inside the kiln. At higher temperatures (1300-1500 °C), melting of the aluminate phase, the ferrite phase and to some extent belite occurs, forming a liquid phase, which leads to solid particles sticking (granulation/nodulization). Further, free CaO and belite react to form alite.^{7,39}

2.2.7 Clinker cooling

Controlled clinker cooling is very important for clinker quality and for the energy efficiency of the overall production process, since it allows heat recovery (Fig. 2-4d). It is essential, that the hot clinker is cooled down quickly to below 1200-1250 °C, as fast cooling causes the re-crystallisation of the finely grained aluminate phase,⁷ which results in a desirable slow, controllable hydration reaction during the setting process of cement. Conversely, a coarsely grained aluminate phase formed due to low cooling rates, causes

overly rapid setting of cement.^{5,45} More important is the effect of rapid cooling on the important alite clinker phase, which is thermodynamically stable only at temperatures above 1250 °C (see Fig. 2-8 in subsection 2.3.2.1). Below 1250 °C, alite decomposes into belite and calcium oxide (Fig. 2-5).^{22,67,68} Fast cooling to temperatures below this critical temperature results in metastable alite.

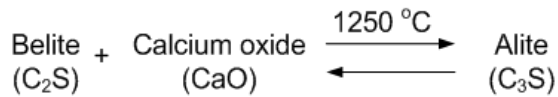


Fig. 2-5: The formation and decomposition reaction of alite.

The clinker is cooled by air flowing through the hot granulated solids. The heated air is recirculated as combustion air (secondary air) into the burner of the rotary kiln (Fig. 2-4e) and/or into the burner of the calcination chamber (tertiary air) (Fig. 2-4f). The higher the cooling rate, the higher the heat recovery and therefore the energy efficiency of the cement production process.^{5,45}

2.2.8 Cement Blending and Grinding

For the preparation of cements, clinker needs to be ground and blended with additives (Fig. 2-3c), the most important of which are gypsum or anhydrite, which control the setting of concrete during hydration. Other additives, depending on the desired cement type, are for example blastfurnace slag, limestone or fly ash.^{5,9,39,69}

2.3 Physio-Chemical Process of Portland Cement Clinker Formation

2.3.1 Clinker Phases

a) Alite (C_3S)

Alite is the most important clinker phase in cement, since it controls mainly the initial and ultimate strength of cement. Portland cement clinker consists of ca. 50-70 wt.% of alite,^{4,7,45} which contains 71-75 wt.% CaO , 24-28 wt.% SiO_2 and 3-4 wt.% substituted ions.⁷ Typically incorporated ions within the alite crystal lattice are Mg^{2+} , Al^{3+} and Fe^{3+} . The impurities in alite stabilize high temperature polymorphs at low temperatures (below

the related decomposition temperature).²¹ So far, there exist seven known polymorphs between room temperature and 1070 °C: three triclinic (denoted with T), three monoclinic (M) and one rhombohedral (R) polymorph (Fig. 2-6).^{7,39,69} Due to incorporations in the alite crystal lattice, M₁ and M₃ polymorphs are present mostly in industrial clinker. Cooling clinker from 1450°C, inversion of the R polymorph to M₃ and further more to M₁ occurs, forming small crystals (M₃) rich in substituents or large crystals, poor in substituted ions (M₁). Especially, high MgO- concentrations promote high nucleation, resulting in formation of small automorphic M₃- crystals.^{7,21} The different polymorphs do not show significant differences in the hydraulic properties.³⁹

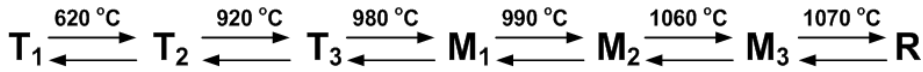


Fig. 2-6: Temperature dependence of the 7 polymorphs of pure tricalcium silicate (alite).⁷

b) Belite (C₂S)

The second largest clinker phase in Portland cement is belite. Its hydration product develops similar strength in cement as alite, only much more slowly. Belite makes up between 15 and 30 wt.% of Portland cement clinker and consists of 60-65 wt.% CaO, 29-35 wt.% SiO₂ and 4-6 wt.% substituted oxides, mainly Al₂O₃ and Fe₂O₃, but also K₂O, Na₂O, MgO, SO₃ and P₂O₅.⁷ Belite crystallizes in five polymorphs: α-belite, α'_H-belite, α'_L-belite, β-belite (H = “high” and L = “low” symmetry) and γ-belite (Fig. 2-7), which differ in structural and hydraulic properties. The α'- polymorphs are the most hydraulic forms of belite, whereas γ-belite is a non-hydraulic polymorph and does not account for the setting and hardening of cement. β-belite is also a hydraulic polymorph, but less hydraulic than the α'- polymorphs. It is the most common polymorph in industrial Portland cement clinker. A phenomenon, that needs to be prevented by trace compounds inclusions, is disintegration (dusting) of clinker, which happens if β-C₂S is not stabilized during cooling and/or by inclusions affording a part β-γ-C₂S inversion. γ-C₂S crystals are less dense (more voluminous) than β-C₂S crystals, which causes cracking of other β-C₂S crystals, forming a voluminous powder and dust.^{7,39}

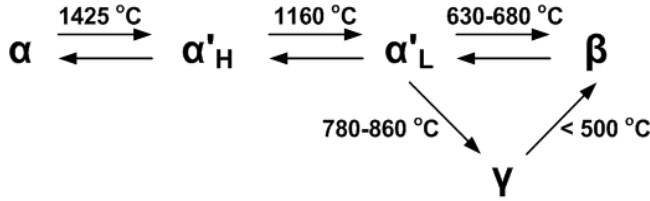


Fig. 2-7: Temperature dependence of the five polymorphs of pure dicalcium silicate.⁷

c) Tricalcium Aluminate (C_3A)

C_3A is the most reactive component of Portland cement clinker, which contains 5-10 wt.% of the phase. Pure C_3A consists of 62 wt.% CaO and 38 wt.% Al_2O_3 and does not exhibit temperature dependent polymorphs. However, ion substitution of Ca^{2+} in the structure of the pure C_3A causes changes in crystal structure. Typically Ca^{2+} is substituted by Mg^{2+} , 2 K^+ and 2 Na^+ , Al^{3+} by Fe^{3+} and Si^{4+} , but only the alkali metals affect the structural changes^{7,39} from a cubic crystal structure (pure C_3A) to orthorhombic and monoclinic structures via intermediate structures of lower symmetry.

In industrial clinker products, orthorhombic and cubic structures are commonly present polymorphs. The orthorhombic form features dark, prismatic crystals, whereas the cubic polymorph forms fine grains with dendritic ferrite crystals.³

d) Calcium Aluminoferrite (C_4AF)

Calcium aluminoferrite constitutes 5-15 wt.% of Portland cement clinker. The pure phase contains 46 wt.% CaO, 21 wt.% Al_2O_3 , 33 wt.% Fe_2O_3 , but in industrial clinker up to 10 wt.% of incorporated oxides appear (mostly MgO). This phase is composed of any solid solution composition of $Ca_2(Al_xFe_{1-x})_2O_5$, with $0 < x < 0.7$ and is typically termed brownmillerite.^{70,71} The denotation C_4AF represents only a single point in this series for $x = 0.5$ (dotted line in Fig. 2-9a) section 3.2). Substitution free C_4AF is yellowish brown, while substituted (Mg^{2+} , Zn^{2+}), air cooled C_4AF is black.^{7,39}

2.3.2 Portland Cement Clinker – a Multiphase Mixture

Depending on the reaction conditions (temperature, pressure, reaction time, composition), a significant variety of phases can be formed from the four major reactants CaO, SiO_2 , Al_2O_3 and Fe_2O_3 of the raw material for Portland cement clinker. Taking additionally

minor compounds into account, the number of stoichiometrically different compositions increases drastically.^{7,72} For the purpose of simplification, the following discussion is based only on reactions of pure CaO, SiO₂, Al₂O₃ and Fe₂O₃, which are also dominating under industrial conditions. These raw materials are also very common in several other industrial products, such as glasses and ceramics, which are produced at temperatures similar to cement clinker (~1400 °C).⁷³ High SiO₂ concentrations in the raw material, for example ~75 wt.%, are typical in glass production, whereas high CaO concentrations, of say, ~70 wt.%, are used to produce cement clinker. This is illustrated in the ternary phase diagram of the CaO-SiO₂-Al₂O₃-system in Fig. 2-8 at a constant Al₂O₃ concentration (dotted line).⁷ At low CaO fraction (~20 wt.%), SiO₂ phases like tridymite or cristobalite (important in glass and ceramic chemistry) occur, while increasing CaO- concentration leads to the appearance of the clinker phases C₃S and C₂S at > 57 wt.% CaO. This shows the importance of high cement raw meal homogeneity. An insufficient high homogeneity, caused for example by poor mixing or too coarse raw material particles (see detailed discussion in subsection 2.3.4.4), could lead to local areas of different chemical composition than the overall composition, potentially causing the formation of product phases other than the typical clinker phases.

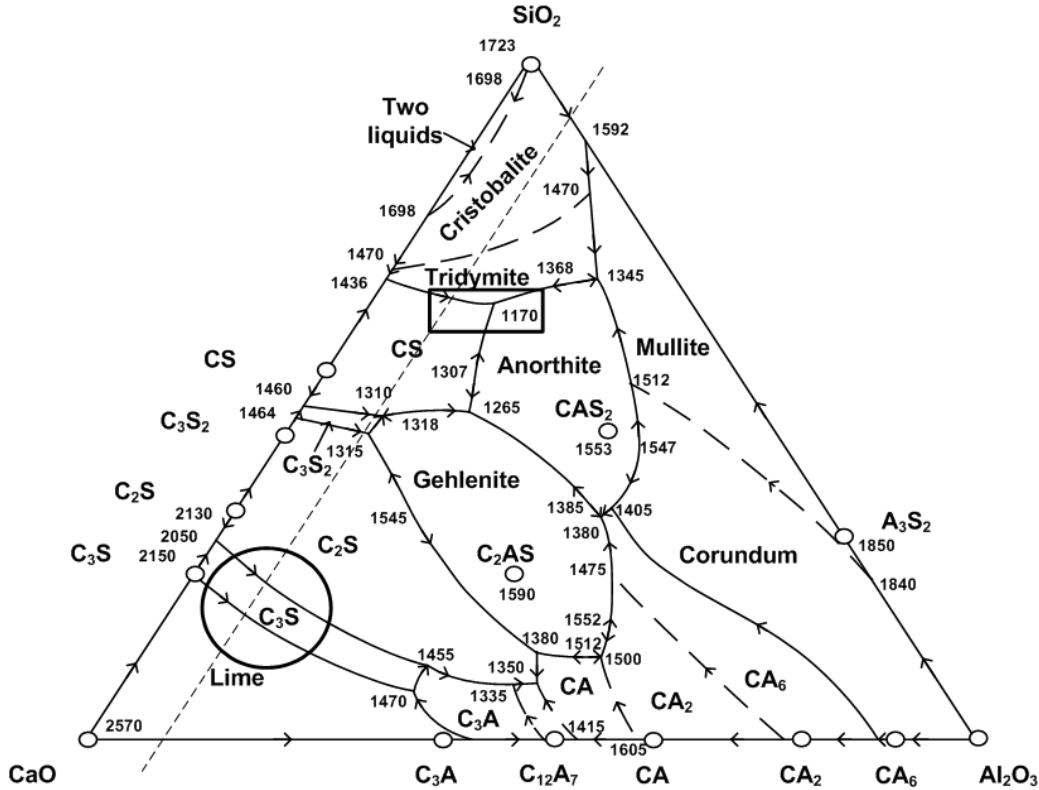


Fig. 2-8: Ternary equilibrium phase diagrams of pure reactants: the CaO-SiO₂-Al₂O₃ system showing the typical Portland cement clinker composition (circle). The area marked by the square denotes the typical composition of these three reactants in Portland cement clinker. Compositions due to inhomogeneities in Portland cement clinker, as denoted by the circle, could result in the formation of a melt phase at lower temperatures, e.g. 1170 °C.^{7,74}

Clinker phase relations are best shown in three- and four-component phase diagrams. The most relevant system is the CaO-SiO₂-Al₂O₃-Fe₂O₃ phase diagram shown in Fig. 2-9a) and the subsystem related to Portland cement clinker (CaO-C₂S-C₁₂A₇-C₄AF) is shown in Fig. 2-9b).^{72,74} It should be pointed out, that this is not an isothermal diagram, which complicates the reading of the diagram. Nevertheless, a few important details are demonstrated. The quaternary phase diagram (Fig. 2-9b) is built up of four ternary systems, which represent the surfaces of the quaternary system: 1) CaO-C₁₂A₇-C₂S, 2) CaO-C₂S-C₄AF, 3) CaO-C₁₂A₇-C₄AF and 4) C₂S-C₄AF-C₁₂A₇. Phase boundaries and

phase fields known from binary and ternary phase systems become surfaces and phase volumes. Two invariant points (P7 and P8), i.e. points where the thermodynamical degrees of freedom are zero, occur in the four-component phase diagram (Fig. 2-9b). At the first invariant point (P7) the solids CaO , C_3S , C_3A and C_4AF co-exist in equilibrium at 1341°C with the liquid phase having a composition of 55 wt.% CaO , 22.7 wt.% Al_2O_3 , 5.8 wt.% SiO_2 and 16.5 wt.% Fe_2O_3 .^{75,76} The second invariant point (P8) is found at 1338°C and the composition of the liquid in equilibrium with the solids C_3S , C_2S , C_3A and C_4AF is 54.8 wt.% CaO , 22.7 wt.% Al_2O_3 , 6.0 wt.% SiO_2 and 16.5 wt.% Fe_2O_3 .^{75,76,77} This point is commonly accepted as a eutectic in this system.^{46,74}

The most important phase volume is the tetrahedron C_3S - C_2S - C_3A - C_4AF (Fig. 2-9c). Any raw meal composition within this phase volume results in the formation of all four major clinker crystal phases for Portland cement clinker. A raw meal composition to the right of this tetrahedron results in the formation of C_3A , C_4AF , C_{12}A_7 and C_2S , but no C_3S , and raw meal compositions to the left of the tetrahedron result in a clinker composition with C_3S , C_3A , C_4AF and free CaO . Both cases are undesirable in cement production. C_2S does not feature the same desired initial strength of a cement paste as C_3S , and is therefore not the preferred main silicate phase in cements, except in special cases such as low energy belite cement. High concentrations of free CaO cause concrete unsoundness, while from an economical point of view remaining high concentrations of CaO are a waste of raw material and energy.

The phase volumes shown in Fig. 2-9b) are primary phase fields. A primary phase field denotes all compositions where a related phase crystallizes first from a melt. This will be explained on the case of C_3S . The primary phase field of C_3S is framed by points P1-P6 in Fig. 2-9b) or by both grey-shaded areas (together) in Fig. 2-9d). This primary phase field superimposes the phase volumes of C_3S - C_3A - C_2S - C_4AF and C_2S - C_3A - C_{12}A_7 - C_4AF (Fig. 2-9d)). The part of the primary phase field superimposing the former one will be regarded as volume 1 (framed by the dark grayish area) and the part superimposing the latter as volume 2 (framed by the light grayish area). First, it is assumed, that the raw meals of any composition in both volumes are completely molten. A decrease in

temperature results in both volumes initially in the crystallization of only C_3S from the melts.

- volume 1: Decreasing the temperature further results not only in the crystallization of more C_3S , but also in phases C_2S , C_4AF and C_3A . At the end of the cooling process, a product is obtained, containing all four solid phases.
- volume 2: Further cooling leads to the crystallization of C_2S , C_3A , $C_{12}A_7$ and C_4AF , while C_3S re-melts. The final composition does not contain the C_3S solid phase, but rather the other four phases.

Consequently, primary phase fields only provide information about the crystallization path of the melt of a given composition. The composition of the final product is not determined by the primary phase fields.

The previous discussion is only valid under equilibrium conditions, which are often not achieved or even desired in industrial processes. For example, rapid cooling of volume 2 compositions prevents the complete re-melting of C_3S , resulting in a product containing C_3S , the most important clinker phase. On the other hand, fast cooling could also result in undesired effects. In this case the white shaded volume (volume 3) on the left side of volume 1 is accounted for (Fig. 2-9d). The primary phase field of CaO joins directly on to the left side of the C_3S primary phase field (Fig. 2-9b), which superimposes partly with the phase volumes of the C_3S - C_3A - C_2S - C_4AF tetrahedron (Fig. 2-9d). The cooling of a melt of any composition in volume 3, results first in the crystallization of CaO . Similar to the scenario described before, CaO re-melts with further cooling, under equilibrium conditions, for compositions of the superimposed zone and the C_3S , C_3A , C_2S and C_4AF phases crystallize. However, fast cooling results in remaining free CaO , decreasing the quality of the clinker product. This discussion is only partly relevant for state-of-the-art cement production, since clinker is only partly formed from melt. But initial attempts have been made to obtain clinker from a completely molten phase.⁷⁸ There it is crucial to use raw meal composition similar to those of volume 1 to avoid either high CaO concentrations (in the case of volume 3 compositions) or high C_2S (and no C_3S) concentration (in the case of volume 2 compositions).

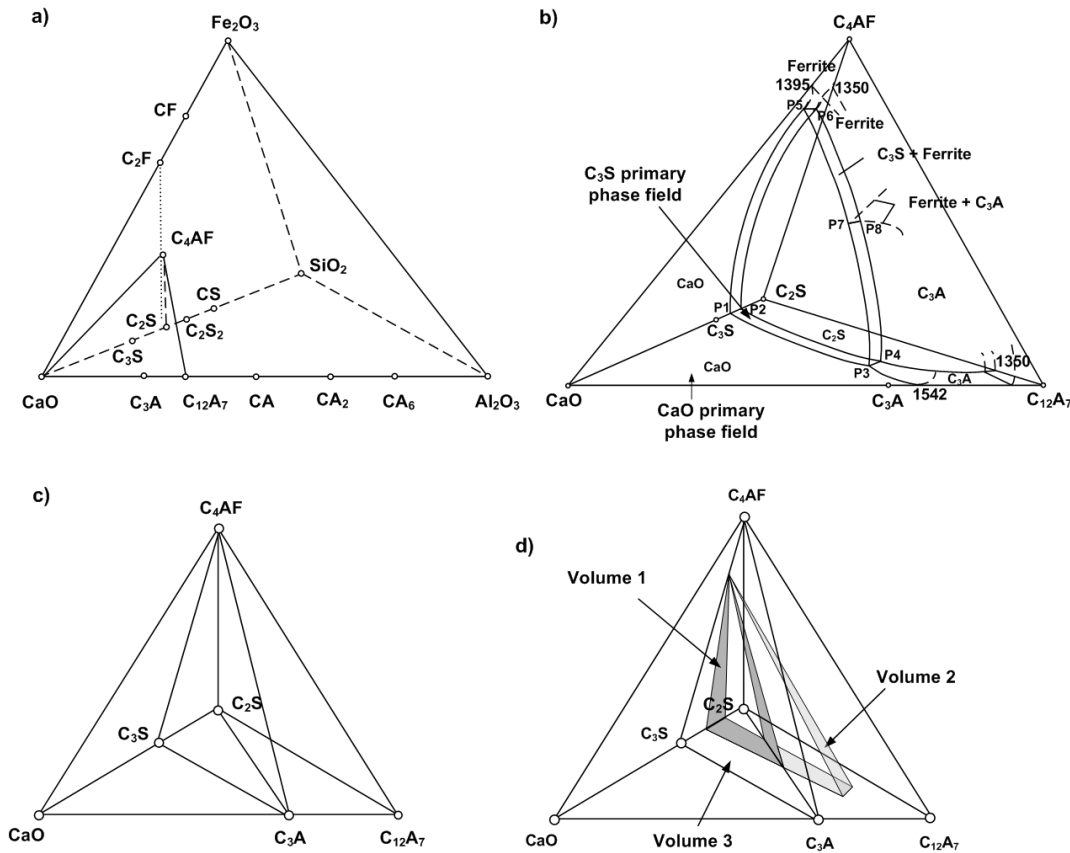


Fig. 2-9: The quaternary phase diagram. a) The CaO-SiO₂-Al₂O₃-Fe₂O₃ phase diagram. The dotted line denotes the variety of ferrite phase compositions. b) The relevant part of a) for Portland cement clinker compositions, showing the primary phase fields of different phases. c) The phase volumes of different clinker phases. d) Primary phase fields and phase volumes of the different clinker phases.⁷²

2.3.3 Clinker Phase related Equations

Based on phase relations in the four component system, several equations have been derived to describe the quality and quantity of Portland cement clinker of a known raw material composition. In all equations the chemical compositions are expressed in wt.%.

The quality of clinker is often referred to as the amount of free (non-reacted) CaO in the sample, which reduces the strength of concrete.³⁹ Up to now many theoretically and empirical derived equations have been developed to calculate the so called “Lime

Saturation Factor (LSF)” (Eq. 1).^{7,72} It is used to quantify the amount of CaO in the raw material that can be combined with SiO₂, Al₂O₃ and Fe₂O₃ to form the main clinker phases C₃S, C₂S, C₃A and C₄AF. For satisfactory clinker quality LSF should be in the range of 92-98%.⁷² A common equation is given in Eq. 1. Other parameters are the “Silica Ratio (SR of Ms)” (Eq. 2) and the “Alumina Ratio (AR or Ma)” (Eq. 3). The SR, usually in the range of 2 – 3, describes the proportion of the silica phases to aluminate and ferrite phases, and reflects the ratio of solid phases (the silica phases) to the liquid phase, formed by aluminate and ferrite, in clinker. AR expresses the ratio between the aluminate phase and ferrite phase and indicates which of these two phases is forming the melt phase (for further details see subsection 4.2.1).⁷

$$LSF = \frac{CaO}{2.8SiO_2 + 1.18Al_2O_3 + 0.65Fe_2O_3} * 100 \quad (\text{Eq. 1})$$

$$SR = \frac{SiO_2}{Al_2O_3 + Fe_2O_3} \quad (\text{Eq. 2})$$

$$AR = \frac{Al_2O_3}{Fe_2O_3} \quad (\text{Eq. 3})$$

A method used to determine the potential quantities of C₃S, C₂S, C₃A or C₄AF from the four major oxides contained in cement raw meal is given by the Bogue calculations^{7,79}, which is only mentioned here for the sake of completeness. Detailed information can be found in ref. ^{7,79}.

2.4 High Temperature Clinker Phase Formation

The mechanisms of the clinker formation process are very complex. The chemical composition of the raw meal controls the quality and quantity of the final clinker product phases, together with raw meal properties like mineralogical composition, particle size distributions and homogeneity, as well as process conditions such as maximum burning temperature and retention time of the material in the kiln.

The formation of the different clinker phases is subject to two or three reaction types: solid state reactions,^{19,80,81} solid-liquid and/or liquid state reactions.²³ Considering Portland cement clinker raw meal composed only of the four major oxides (CaO, SiO₂, Al₂O₃ and Fe₂O₃) in a pure form, reactions below 1250 °C proceed solely via solid state reactions. In an absolutely homogeneous mixture, no liquid phases are formed below 1338 °C, where a eutectic in the four component system exists. Nevertheless, due to inhomogeneities, small amounts of melt occur locally at temperatures below 1338 °C. It is assumed that at temperatures above 1325 °C enough melt exists to wet most of the remaining solid particles, in which case mainly solid-liquid or liquid-liquid reactions occur. Between 1250 and 1325 °C all three reaction types exist simultaneously.¹⁶ Of course these absolute temperature values are not strictly valid, since the occurrence of melt depends highly on the actual composition, including minor compounds, and the degree of inhomogeneity of each raw meal mixture. As an example, most of the belite phase and the aluminate as well as ferrite phase formation occur below around 1250 °C via solid-solid interactions, whereas alite is formed by all three reaction types above 1250 °C. Compared to reactions in the presence of a liquid phase, solid state reactions always proceed between two compounds only, whereby the product is formed at the original phase boundary between the solids. Diffusion is the fundamental prerequisite for solid-solid reactions.^{82,83} It occurs due to crystal lattice defects (Fig. 2-10a) and proceeds in two basic steps (Fig. 2-10b) namely self-diffusion of the diffusing species (e.g. Ca²⁺ in CaO) and diffusion through the product layer toward the reaction interface.^{82,83} A critical role in the rate of reaction is the contact made by the solid particles.

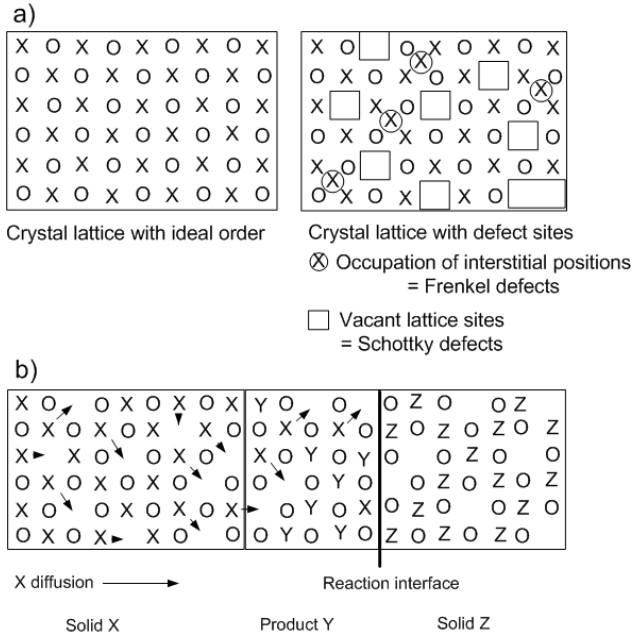


Fig. 2-10: a) Draft of a crystal lattice. X represents cations and O anions. The ideal order is shown on the left side and the lattice exhibiting defect sites are shown on the right side. Important crystal lattice defects are vacant sites and the occupation of interstitial positions⁸². b) A sketch of X-ions diffusion through solids. Diffusion through solid X represents the self-diffusion of X-ions. This is followed by the diffusion of X through a newly formed product layer Y. At the interface between product Y and solid Z the reaction occurs and more Y is formed. The reaction interface moves in the direction of solid Z.

In the clinkerization process the four possible diffusing ion species found are Ca^{2+} , Si^{4+} , Al^{3+} and $\text{Fe}^{2+}/\text{Fe}^{3+}$. These dominating diffusion species are often determined by a comparison of the activation energies of different clinker formation reactions with the activation energies for species self-diffusion.^{20,84,85} In a more accurate method, platinum markers are utilized in clinker formation experiments with pressed powder compacts, which are assembled from two annealed specimens, each containing one of the pure oxides (Fig. 2-11).^{18,19,86,87} The marker is positioned at the phase boundary between the compacts. After the clinkerization experiments an evaluation was made as to which side of the marker the product was located. In the example shown in Fig. 2-11 the powder compact is assembled from a CaO specimen and a SiO_2 specimen. After the

clinkerization reaction takes place, the marker is located at the boundary phase between CaO and the C₂S (Ca₂SiO₄) product. Similar tests were carried out in the CaO-Al₂O₃ system.⁸⁷ These experiments reveal clearly the higher mobility of Ca²⁺ cations. The only exception arises in the case of ferrite phase formation (C₄AF; Ca₄Al₂Fe₂O₁₀), in which Fe³⁺/Fe²⁺ is the major diffusing species.⁸⁵

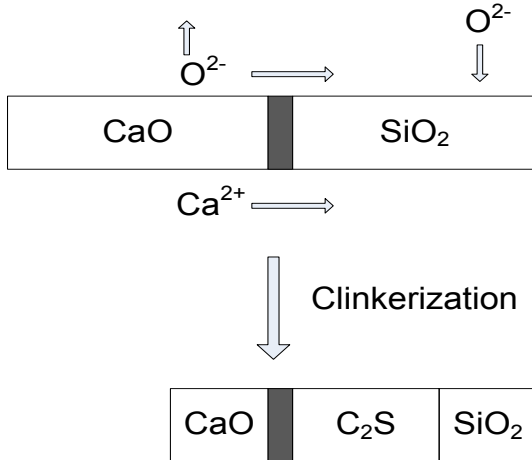


Fig. 2-11: Determination of the diffusing species in the CaO-SiO₂ system utilizing marker experiments. A platinum marker is positioned between two compacts of pure raw material. After clinkerization the location of the marker is evaluated. Since it is found between the CaO compact and the newly formed product layer, Ca²⁺ is assumed to be the dominating diffusing species. As a consequence of electroneutrality, “O²⁻” diffusion through the solid or transport through the gas phase occurs.^{20,86}

In the following sections of this article, the formation of the four main clinker phases is discussed. The order of the sections is orientated around the order of the clinker phase occurrence in the industrial process for temperatures of 900 °C up to 1500 °C: belite, aluminite, ferrite > melt > alite. The influence of the particle size distribution is subsequently discussed.

2.4.1 Clinker Phase Formation between 950 and 1250 °C

a) Belite (C_2S) Formation

In industrial cement production belite is formed in the rotary kiln at 900-1250 °C.¹⁵ Although the process in the kiln is complex and depends on many parameters the basis of belite formation is the reaction between solid CaO and SiO₂ particles. Therefore, it can be described by reactions of the two pure oxides only. The basic understanding of belite formation was established in the 1920s and 1930s^{80,81} and has been verified in later investigations utilizing advanced analysis techniques.^{15,18-20} In the reaction of pure CaO and SiO₂, belite is one product, with others being: C_3S_2 ($Ca_3Si_2O_7$) and CS ($CaSiO_3$) at temperatures between 950 and 1450 °C, and in the case of CaO- excess, and temperatures above 1250 °C, alite also (C_3S ; discussed later). Of these phases, only C_2S and C_3S are of interest, since the other do not exhibit hydraulic properties. The formation of the different phases is determined by diffusing Ca^{2+} through solid matter, which is dependent on temperature, the concentration of the two compounds and on the methods used to prepare the raw meal. In solid-solid reactions, the product occurs as a layer between the original raw materials.

Belite (C_2S) is the favored formed product phase in the case of CaO- excess.^{19,19,80,81} In investigations concerning the influence of CaO and SiO₂ concentration, the C_2S concentration was found to be higher with an increasing CaO/SiO₂ molar ratio in the raw meal mixture. In raw mixes of CaO/SiO₂ molar ratios of 4:1 or 3:1 belite have been the only product phase formed. Decreasing CaO concentration, i.e. to CaO/SiO₂ = 1:1 or 1:2, causes the formation of additional silicate phases, C_3S_2 and CS, while the formation of belite exhibits a maximum concentration, and a decrease with time, until no belite is left. It has been concluded, that C_2S is the first phase formed in the presence of CaO-excess at the interface of the CaO and SiO₂ solids. At longer reaction times [CaO] decreases and therefor Ca^{2+} -diffusion through the product layer. The more acidic phases C_3S_2 ($Ca_3Si_2O_7$) and CS are also formed at the interface of C_2S and SiO₂.^{18,81,81} With the total consumption of CaO, the $[Ca^{2+}]$ at the CaO/ C_2S phase boundary becomes low and C_2S -formation stagnates. Finally, Ca^{2+} -diffusion occurs only from the product phases rich in CaO in the direction of any remaining SiO₂. Here, more CS is formed at the CS/SiO₂

interface. The diffusion of Ca^{2+} decreases CaO concentration in C_2S and C_3S_2 , with the former transforming into C_3S_2 and the latter into CS. Therefore, [CS] increases at the cost of other phases (Fig. 2-12).⁸¹ The complete conversion of C_2S to CS is a slow process and takes, even for raw meal mixes with low [CaO], up to 18 hours.⁸¹ Considering this time frame, the conversion of C_2S to CS does not play a major role in the industrial process, since the residence time of the reactants in the kiln is 60 minutes maximum.

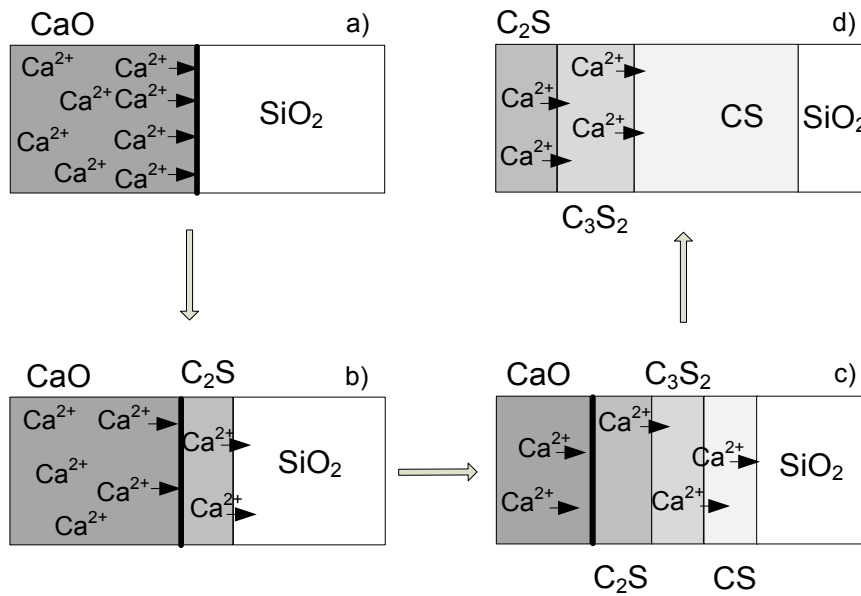


Fig. 2-12: Formation of C_2S by solid-solid reactions. a) A high concentration of Ca^{2+} -diffuses towards SiO_2 . b) At the interface C_2S is formed, and the product phase grows. c) The concentration of Ca^{2+} decreases. Less CaO rich phases, C_3S_2 and CS, are formed. d) CaO is completely consumed. Ca^{2+} -diffusion occurs only in the formed product phases. CS is formed at the cost of C_2S and C_3S_2 .

Higher temperatures increase the mobility of diffusing species, and thereby accelerate the clinker formation reaction. Analogous results were reported by Weisweiler et al.¹⁸, who established that an increase in temperature from 1000 to 1250 °C increased the reaction rate constant of C_2S formation by a factor of 75.¹⁸ The increase of the Ca^{2+} -diffusion is attributed to a higher number of disordered ions and vacant sites in the crystal lattice with increasing temperature, and to an increase in the number of mobile Ca^{2+} -ions.⁸²

Besides the diffusion rate, the temperature also influences the conversion of belite polymorphs. High temperature *in situ* XRD studies enables the tracking of belite polymorph conversions during the reaction:¹⁵

- at 950 °C belite exists as a α'_L -C₂S polymorph
- up to ~1055 °C, the transformation of the α'_L -C₂S polymorph to α'_H -C₂S is completed
- complete conversion into the α -C₂S polymorph occurs at 1380 °C, but during the cooling process this transformation proceeds in a reversed way and is completed at 1240 °C.

In diffusion controlled reactions, the diffusion distance of a species significantly influences the rate of the reaction. In powdery raw meals the diffusion distance to the reaction interface depends on the fraction of particle fines, and is expressed by the surface/volume ratio. The higher the ratio, the shorter the diffusion distance, in general. Comparisons of raw meal powder samples ground in a mortar for 15 and 150 minutes, respectively, have shown a drastic increase in the reaction rate of the CS formation when increasing treatment time. C₂S-formation reaches its maximum concentration earlier and the formation of C₃S₂ as well as CS starts earlier. The conversion of C₂S is completed four times faster than in the case of shorter grinding treatment.⁸¹ Although these results were not discussed further by Jander *et al.*, they can be attributed firstly to an increased homogenisation of the powder mixture and secondly to an increase of particle fineness, i.e. an increase in the surface/volume ratio. Investigations comparing the reaction rate of raw meal mixes containing CaCO₃ or CaO have shown similar results.⁸⁰ In the case of the use of CaCO₃, the complete reaction to CS was faster than when using CaO. The pre-calcined CaO featured larger particle sizes than the original CaCO₃ particles,⁸⁰ which caused an increase in the diffusion distance. Similar results have been obtained by varying the SiO₂ particle size.⁸⁰ Although these results concerned CS-formation, the same correlation of raw material particle size with the diffusion rate, respectively the reaction rate, is valid, because each CS-formation precedes C₂S-formation. A more detailed discussion about the influence of particles sizes on the clinker phase formation will be given later in the text.

In the industrial process a typical raw meal composition consists of 64.4 wt.% CaO, 20.1 wt.% SiO₂, 6.3 wt.% Al₂O₃ and 2.4 wt.% Fe₂O₃ (LSF=99, SR=2.3, AR=2.6) excluding minor compounds.⁵ Belite formation often begins in the pre-calcliner at around 900 °C, and continuous in the rotary kiln.¹⁵ The reaction of CaO and SiO₂ at the particle interface causes the formation of the belite polymorph $\alpha'_L\text{-C}_2\text{S}$ (Fig. 2-13a).¹⁵ The formed product layer is not a rigid uniform crystal layer, but consists of fine, packed belite crystals.^{23,8799} Further Ca²⁺ diffuses through the newly formed product layer, and reacts at the phase boundary between the product and SiO₂ particles (Fig. 2-13b). The continuous Ca²⁺-diffusion causes an increase in belite layer thickness, while the SiO₂ particle core shrinks simultaneously (Fig. 2-13c). In addition, the belite crystals grow in size mainly by coalescence.⁸⁸ Besides the formation of the product layer a stepwise transformation of the belite polymorphs occurs simultaneously. At circa 1055 °C the $\alpha'_L\text{-C}_2\text{S}$ polymorph is completely converted into $\alpha'_H\text{-C}_2\text{S}$.¹⁵ The belite formation reaches its maximum (ca. 60 wt.%) at around 1250 °C. Above 1250 °C most of the belite is consumed due to the formation of alite. The remaining $\alpha'_H\text{-C}_2\text{S}$ is converted at higher temperatures in the more reactive polymorph $\alpha\text{-C}_2\text{S}$.⁸⁹ It should be mentioned here that during clinker cooling belite polymorph transformation occurs in the opposite direction and the $\alpha'_L\text{-C}_2\text{S}$ polymorph and $\beta\text{-C}_2\text{S}$ are most likely contained in the final clinker product.⁸⁸

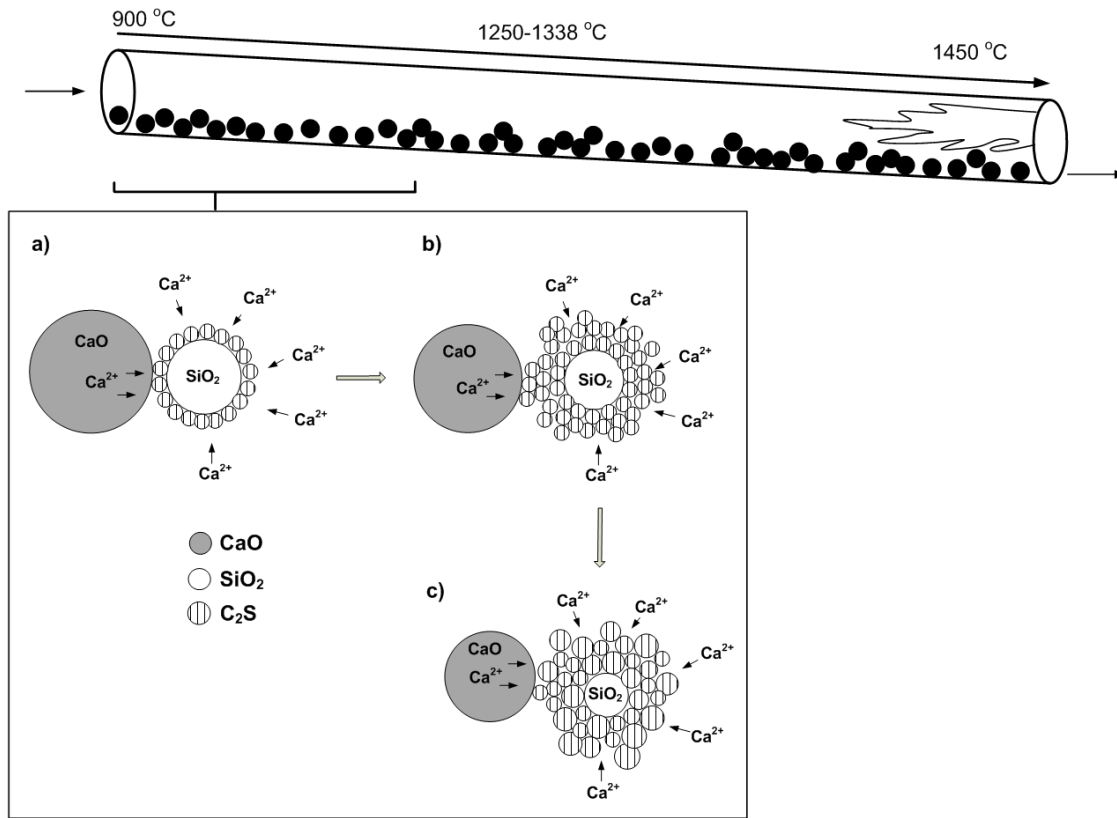


Fig. 2-13: C_2S formation in particles. a) A layer of C_2S crystals is formed at the interface of CaO and SiO_2 . b) With the further diffusion of Ca^{2+} towards SiO_2 , more C_2S crystals are formed. Simultaneously, the SiO_2 particle shrinks. c) C_2S crystals grow in size due to coalescence.

b) Aluminate (C_3A) and Ferrite (C_4AF) Formation

C_3A and C_4AF are of particular importance in the clinkerization formation, as these phases form a molten phase at lower temperatures, which influence the development of the chemical and physical properties of the final clinker product greatly.⁹⁰ The formation of C_3A and C_4AF occurs in three steps:

1. between 950 and 1250 °C the crystalline phases C_3A and C_4AF form
2. above 1250 °C, the crystalline phases melt
3. re-crystallization during clinker cooling.

Here, the focus will be on the first steps only, as the second step will be outlined in subsection 2.3.4.2.1. The re-crystallization process is thoroughly described elsewhere.⁹¹

The formation of the C_3A and C_4AF phases will be described only by reference to the reaction between CaO , Al_2O_3 and Fe_2O_3 .⁹²

Tricalcium Aluminate (C_3A) Formation

In the solid-solid reaction of CaO with Al_2O_3 , several calcium aluminate phases could in principle be formed, including: C_3A , $C_{12}A_7$, C_2A , CA , CA_2 and CA_6 .^{15,84,87,89-101} As discussed earlier, the occurrence of a phase, and the phase formation sequence, strongly depends on experimental conditions, i.e. the concentration of the raw materials, temperature, particle size, particle contact pattern and the extent of crystal lattice defects within the reactants. An overview of possible formation paths is given in Fig. 2-14.

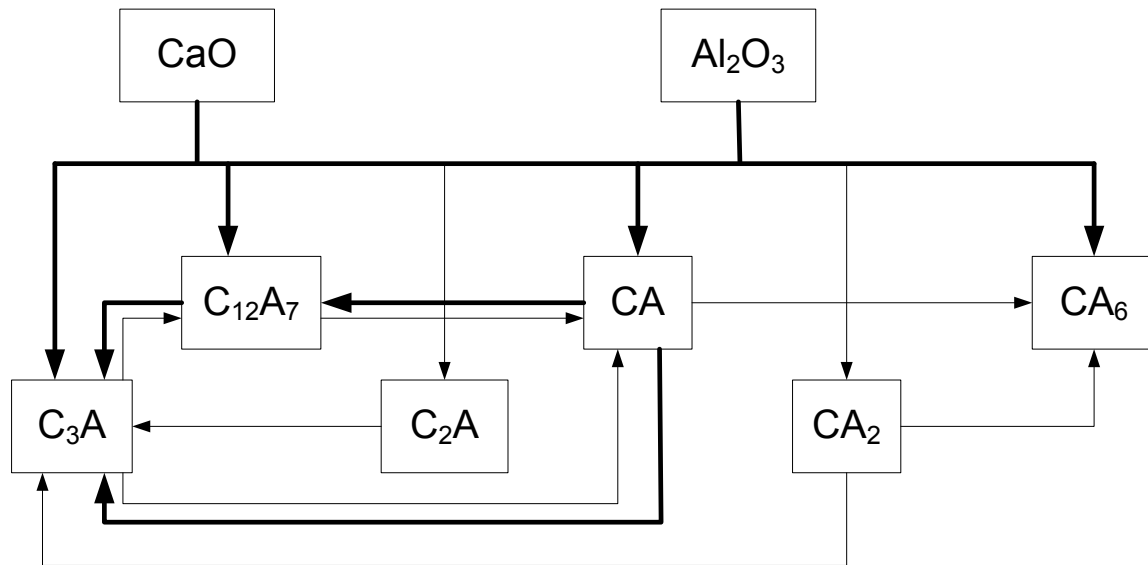


Fig. 2-14: The formation of aluminate phases. The most important aluminate phase in Portland cement clinker is C_3A , which is formed by the direct reaction of CaO and Al_2O_3 or previously formed intermediate phases like $C_{12}A_7$, C_2A , CA , CA_2 . CA_6 is a by-product. Bold arrows indicate the favored direction of equilibrium reactions.

Some general conclusions on the formation of the C_3A phase, i.e. the phase of interest in Portland cement clinker, can be drawn. In general, the dominantly diffusing species is Ca^{2+} (Fig. 2-15), although Al^{3+} diffusion also occurs to a small extent.^{87,98} Occurring phases are formed as layers between CaO and Al_2O_3 .

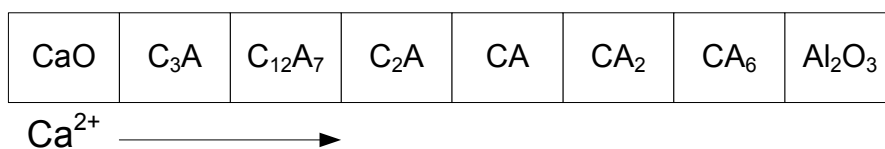


Fig. 2-15: The order of aluminate phases formation because of the direction of Ca²⁺-diffusion towards Al₂O₃ (indicated by the arrow). CaO rich phases are formed close to CaO and Al₂O₃ rich phases on the opposite side.

In most investigations the C₁₂A₇ phase was initially formed,^{84,87,92,95,96} while in some cases this also applied to the CA or CA₂ phases.^{87,92,95} The final product depends, analogous with belite formation, on the concentration of CaO and the CaO/Al₂O₃ molar ratio, respectively. An excess of CaO, results in the formation of C₃A,⁹⁴⁻⁹⁶ while any deficiency in CaO causes the formation of Al₂O₃ rich phases.^{87,97,99}

Higher temperatures accelerate the diffusion of Ca²⁺ due to an increase in the number of mobile Ca²⁺ ions and a higher number of defect sites in the crystal lattice, respectively.^{87,93,96,97}

In the CaO-Al₂O₃ system “mechanochemical activation” has been studied.^{95,96,99,100} This term describes the increase in the reactivity of solids due to mechanical treatment, e.g. grinding, which is not related to particle size effects.¹⁰¹ Mechanical stress on a crystal lattice causes distortion and deformation of the crystal structure¹⁰¹ and an increase of crystal defect sites.^{95,96} In the case of aluminate phase formation, ball-milled raw materials feature reaction rate acceleration of the desired phase, governed by the CaO/Al₂O₃ ratio, especially at lower temperatures (~1100 °C) compared to raw materials, which are not mechanically pre-treated. Similar to the effect of higher temperatures, the increase of defect sites in the crystal lattice of the raw materials enhances Ca²⁺- cations diffusion and therefore product formation.^{95,96,99} The study of this mechanochemical activation for clinker formation is still in its infancy. Further investigation needs to be focused especially on the significance of the reaction rate increase due to mechanochemical activation compared to the increase of the reaction rate due do a decrease of particle sizes by grinding (mechanical treatment).

Tetracalcium Aluminoferrite (C_4AF) Formation

In situ synchrotron powder diffraction of the clinkerization reactions indicates the consumption of C_3A when forming the ferrite phase C_4AF with Fe_2O_3 .¹⁵ The concentration of C_4AF increases up to approximately 20 wt.%, while the concentration of C_3A decreases. As soon as the ferrite-phase reaches a constant level at around 20 wt.%, the C_3A concentration increases again. The ferrite phase C_4AF is formed by the reaction of C_3A with Fe^{3+}/Fe^{2+} or with phase CF ($CaFe_2O_7$), which is also formed in a CaO - Al_2O_3 - Fe_2O_3 system.⁸⁵ The former reaction is the preferred option of the two; therefore Fe^{2+}/Fe^{3+} ions diffuse into the aluminate phase and replace Al^{3+} -ions. If all free iron oxide is consumed, the reaction of C_3A with CF occurs (at lower temperatures of circa 1100 °C). At temperatures greater than 1100 °C the CF phase disproportionates into C_2F and CF_2 phases. These phases form in a side reaction with C_3A and CaO more C_4AF . An overview of the ferrite phases is given in Fig. 2-16.

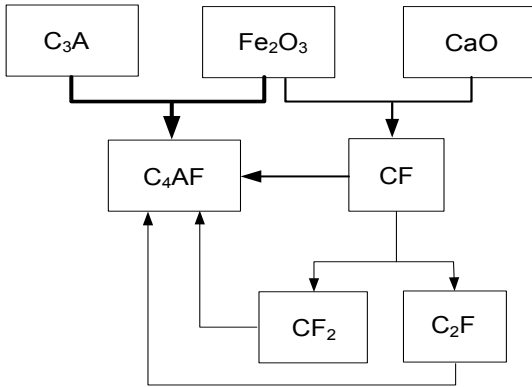


Fig. 2-16: The formation of the C_4AF phase. C_4AF is formed directly due to the reaction of C_3A with Fe_2O_3 or from intermediate ferrite phases like CF , CF_2 and C_2F .

C_3A and C_4AF phase formation starts after the calcined raw materials enter the rotary kiln (Fig. 2-17). At the phase boundary between the CaO and Al_2O_3 particles, the intermediate phase $C_{12}A_7$ is formed. With increasing temperature, due to the motion of the solid materials along the kiln, Ca^{2+} diffusion is enhanced. At the interface between the CaO particles and the $C_{12}A_7$ crystals, C_3A is formed at the cost of $C_{12}A_7$. As a side reaction to C_3A - formation, C_4AF - formation occurs. Fe_2O_3 particles are in contact with the freshly formed C_3A . Fe^{3+}/Fe^{2+} -ions diffuse into the aluminate phase and partly replace Al^{3+} ions

in the crystal lattice. At this stage, i.e. $\sim 1050 - 1200^\circ\text{C}$, both C_3A and C_4AF are formed simultaneously. The concentration of C_4AF increases steadily, whereas C_3A concentration remains nearly constant, due to consumption for the formation of the former phase.¹⁵ At the end of this step, i.e. the formation of the crystalline phases, the concentration of C_3A reaches around 12 wt.% and C_4AF circa 7 wt.% for the same raw meal composition used for the example in subsection 2.4.1a).⁵

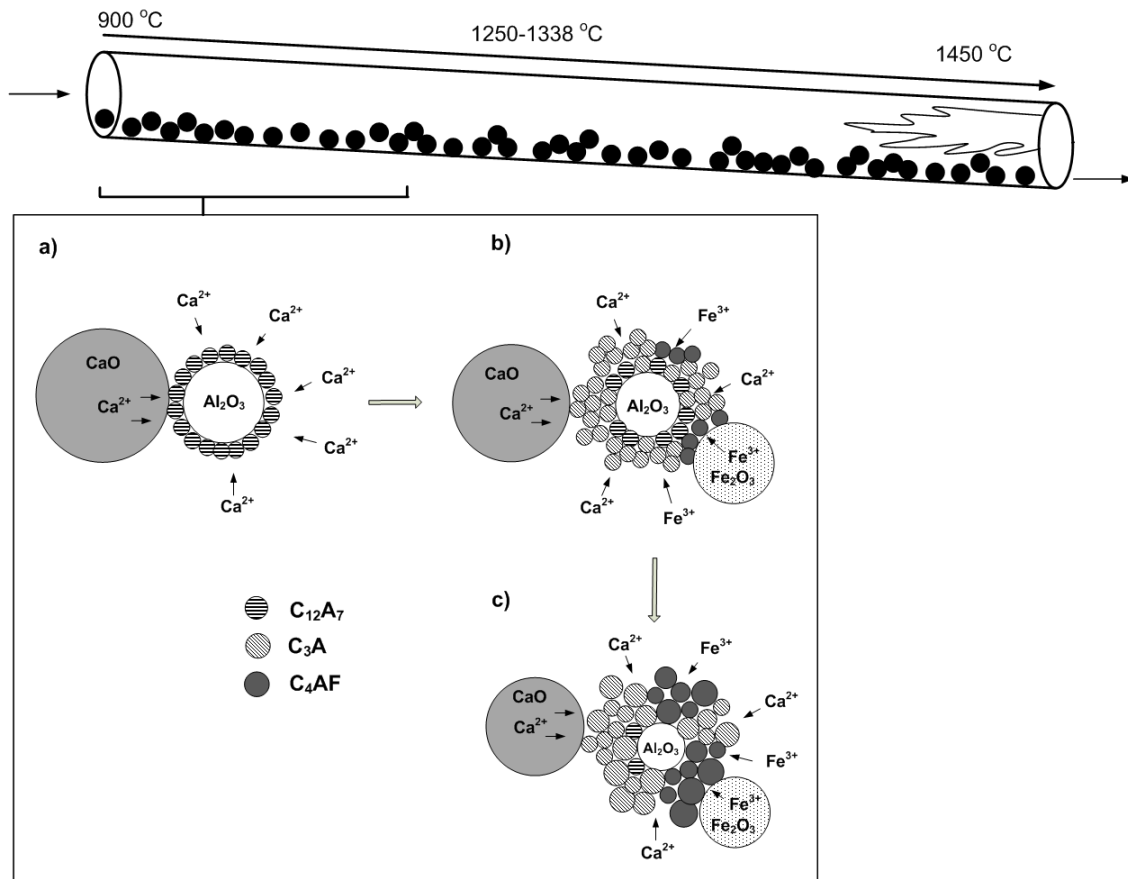


Fig. 2-17: Aluminate and ferrite phase formation. a) Ca^{2+} cations diffuse results in the formation of the intermediate phase C_{12}A_7 at the interface of CaO and Al_2O_3 particle. b) The aluminate phase is formed due to further diffusion of Ca^{2+} and a reaction with the previous formed intermediate phase. Fe^{3+} cations penetrate the formed aluminate phase causing the formation of the ferrite phase. c) Growing aluminate and ferrite crystals and consuming Fe_2O_3 , CaO , Al_2O_3 and C_{12}A_7 .

2.4.2 Clinker Phase Formation between 1250 and 1450 °C

a) Liquid Phase Formation

In systems consisting of only CaO, SiO₂, Al₂O₃ and Fe₂O₃, with typical Portland cement compositions, melting C₃A and C₄AF crystal phases commences at the eutectic at 1338 °C.^{15,75,76} This is only valid in an absolutely homogeneous mixture. Inhomogeneities in the raw meal mixture cause a shift of the eutectic toward lower temperatures (and different compositions). As an example, local composition in an Portland cement raw meal mix of 23 wt.% CaO, 15 wt.% Al₂O₃ and 62 wt.% SiO₂ melts at a temperature of circa 1170 °C (section 2.3.2 Fig. 2-8 square).¹⁰ In addition, all natural raw materials contain minor compounds, which decrease the melting point of a certain composition. Therefore it is common, that a molten phase occurs in industrial raw meal mixes at temperatures lower than 1338 °C. Actually, de la Torre et al. observed the melting of C₃A and C₄AF at 1280 °C through *in situ* studies of clinker formation.¹⁵ To simplify, the following discussion of melt formation will be described for a homogeneous system of pure oxides at a temperature of 1338 °C. The reader should keep in mind, that temperatures might shift by 50-100 °C in more typical Portland cement raw meals.

The composition of the melt phase at the eutectic point is 54.8 wt.% CaO, 22.7 wt.% Al₂O₃, 16.5 wt.% Fe₂O₃ and 6.0 wt.% SiO₂. Preformed crystalline C₃A and C₄AF melt to provide Al₂O₃ and Fe₂O₃, as well as CaO for the melt phase. SiO₂ is obtained from free SiO₂ particles or, if all has been consumed for belite formation, partially molten crystalline belite (Fig. 2-19a-c). The extent of C₃A and C₄AF melting at 1338 °C depends on the total clinker raw meal composition, i.e. on the ratio of Al₂O₃/Fe₂O₃ in the total composition. This can be visualized in Fig. 2-18, which shows the part of interest for Portland cement clinker compositions in the phase diagram for the four oxides. Since only C₃A and C₄AF melt, the amount of all the other phases, i.e. mainly CaO and C₂S is fixed. It should be emphasized here, that for all three of the following discussed cases, the Al₂O₃/Fe₂O₃ ratio of the molten phase is always 1.38, as it is for the eutectic composition. In the first case, a total clinker raw meal composition with an Al₂O₃/Fe₂O₃ ratio of 1.38 is considered. The total composition can be described by the triangular plane CaO-C₂S-P8 in Fig. 2-18. The Al₂O₃/Fe₂O₃ ratio is constant over the whole surface of the plane.⁷⁶ Since it is the same ratio as in the molten phase at the eutectic, all crystalline C₃A and

C₄AF melts.¹¹ A total raw meal composition with an Al₂O₃/Fe₂O₃ ratio less than 1.38 is represented by any triangular plane between CaO-C₂S-P8 and CaO-C₂S-C₄AF. In this case, Fe₂O₃ exists in higher concentrations - as in the previous case and therefore more crystalline C₄AF is formed. When melting commences C₃A melts completely, but only parts of C₄AF melt to provide the melt phase with 16.5 wt.% Fe₂O₃ (eutectic Fe₂O₃ concentration). The other part of C₄AF remains crystalline. Finally, an Al₂O₃/Fe₂O₃-ratio higher than 1.38 in the total raw meal composition is considered, which is described by every plane between CaO-C₂S-P8 and CaO-C₂S-C₁₂A₇. Here, the case is reserved. More Al₂O₃ exists in the raw meal than in the first case, so more C₃A is formed and the amount of C₄AF is limited, which results in the complete melting of the ferrite phase, while only parts of the aluminate phase melt.^{11,76} Crystalline C₃A is left.

Fig. 2-18: Melt formation from C_3A and C_4AF . Point P8 denotes the eutectic in the quaternary system. The Al_2O_3/Fe_2O_3 - ratio at this point is 1.38. The scattered triangle, swinging around the $CaO-C_2S$ axis, represents a constant CaO and C_2S composition. For any position of the scattered triangle between points C_4AF and P8, the Al_2O_3/Fe_2O_3 - ratio is <1.38 indicating a complete melting of C_3A . The Al_2O_3/Fe_2O_3 - ratio for any position of the triangle between point P8 and $C_{12}A_7$ is >1.38 , indicating a complete melting of C_4AF .⁷²

The liquid phase fulfills two important tasks in the clinker burning process:

- 1) acceleration of the clinker phase formation and
- 2) prevention of clinker dust formation.

This results in the macroscopic effect of nodule formation. In clinker nodules solid raw material particles as well as formed crystal phases are held together by the liquid phase. Further crystal phase formations are accelerated due to the diffusion of Ca^{2+} through the melt, which is faster than diffusion through solids.²⁴ Strong agglomerates are formed, when melt is present, around 15 - 20 wt.% filling out most of the void space between particles.⁹ The amount of ungranulated material increases with a decrease of liquid, since less particles are moistened by the liquid.¹⁰²

The granulation proceeds in three steps:

- 1) agglomeration and re-grouping of the particles,
- 2) granule growth and
- 3) solidification and crystallization of the melt.^{12,102}

The first step occurs rapidly. Primary particles are moistened by droplets of liquid, which are then quickly drawn and held together to form porous granules (Fig. 2-19d). Small granules have an excess of liquid at their outer boundaries, so more particles can be incorporated in the granule.¹⁰² Denser agglomerates are formed by re-grouping grains (Fig. 2-19e). The melt enters the pores in and between the agglomerated particles, and carries weakly bound particles into the interior which is accommodated by particle shrinkage. This process is strongly dependent on the surface tension and viscosity of the liquid,^{12,102} but independent of rotational speed of the kiln, retention time in the kiln or material loading.¹⁰³ A high surface tension is required to ensure sufficient adhesion of the particles to each other and a lower viscosity supports particle transport. It was found by Timiashev *et al.*¹³, that the final size of clinker nodules is directly proportional to the surface tension of the melt. In this context the effect adding minor compounds is of great importance. Pure cement clinkers exhibit surface tensions of ca. 0.5 N/m (comparable with the surface tension of Hg) and a viscosity of 0.1 - 0.2 Pa·s (similar to the viscosity of olive oil). The second stage of the nodulization is characterized by granule growth and the formation of the crystal phases C_2S and C_3S (Fig. 2-19f).^{12,102} Therefore alite is surrounded by more melt than belite, since it develops a less dense crystal packing.¹⁴ This

stage becomes dependent on time, rotational velocity and loading, while inertial and gravitational forces become important with the tendency for granules to break down, counteracting growth.¹⁰² In the third stage the liquid crystallizes to form the aluminite and ferrite phase at a temperature of ~ 1250 °C¹⁵ or, if the liquid cools down too rapidly, it forms a glass residue.^{75-77,79}

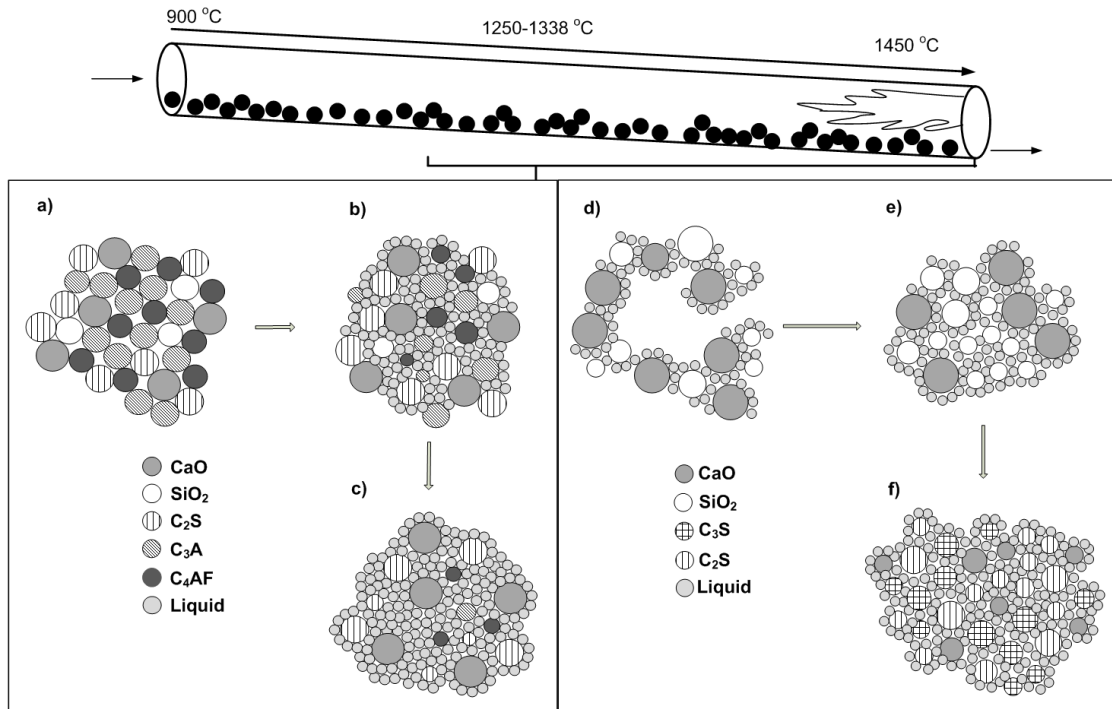


Fig. 2-19: Melt and granules formation. a) The clinker consists of crystalline phases in a four-oxide system until temperatures between 1250 and 1338 °C are reached. b) At the beginning of the melt formation C_3A , C_4AF and SiO_2 melt. c) C_2S melts partially if all free SiO_2 is consumed completely. d) The CaO and SiO_2 particles are moistened by the melt and form porous granules. e) Denser granules are formed, due to smaller particles re-grouping into the interior of the granule. f) The granules grow and the clinker phases C_3S and C_2S are formed.

b) Alite (C_3S) Formation

The alite crystal phase is the preferred clinker phase in Portland cement clinker, since it features the highest hydraulic strength. The formation of alite is very complex, since it can proceed via solid-solid-²⁰, solid-liquid-⁹⁰ or liquid-liquid-^{21,23} reactions. Mostly, the

solid-solid reaction can be neglected, since diffusion through solids is minimal compared to diffusion through a liquid.²³

Alite is only formed in the presence of excess CaO, i.e. at $\text{CaO/SiO}_2 > 1$, and is thermodynamically stable above 1250 °C.²¹ Small amounts are already formed at lower temperatures and therefore the belite and alite formation overlap, which complicates the kinetic description.⁸¹ The formation reaction is believed to be controlled by the diffusion of Ca^{2+} , through the liquid phase.^{9,17,23-26} CaO dissolves partly in the melt, and Ca^{2+} ions diffuse in the direction of the belite product, where the formation reaction occurs. Nonetheless, it is not investigated in detail, whether the belite phase melts and C_3S crystallizes out of the melt or if the solid belite is converted into alite by penetration of Ca^{2+} into defect sites of the solid C_2S (Fig. 2-20a).²³

Nevertheless, the new alite crystals form layers between the CaO agglomerates and belite crystals (Fig. 2-20b). The alite crystal layer is not rigid and the void between the crystals is filled with liquid. Successive Ca^{2+} diffusion occurs through the alite crystal/melt layers to the interface between alite and belite. Although the reaction boundary is located away from CaO, the alite layer functions as a connection to the CaO agglomerates due to the inner motion of the liquid (Fig. 2-20c)). Decreasing CaO concentration during the continuing process results in the growth of alite crystals instead of forming new seed crystals.²³ The consumption of CaO during the alite formation could result in pores of the size of the original CaO agglomerates, surrounded by a product layer.²⁶ Advanced diffusion studies in the ternary system $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ show the correlation between the reaction rate for the alite formation and the amount of liquid phase. A fourfold increase of the melt up to 30 wt.% in the clinker mixture, increases the reaction rate by a factor of about 13 at a temperature of 1500 °C. Although this investigation considered only isothermal conditions, the finding can also be applied correspondingly to non-isothermal conditions in industrial clinker production.¹⁷ The nature of the reaction rate increase has not yet been discussed, but it might be related to an increase in the number of solid particles, in this case CaO and belite, being in contact with liquid. The macroscopic effect is the formation of strong nodules as described above.¹⁰² The increased contact surface between the two phases increases the number of diffusing species (Ca^{2+}) penetrating through the interface into the belite phase, where alite formation occurs.

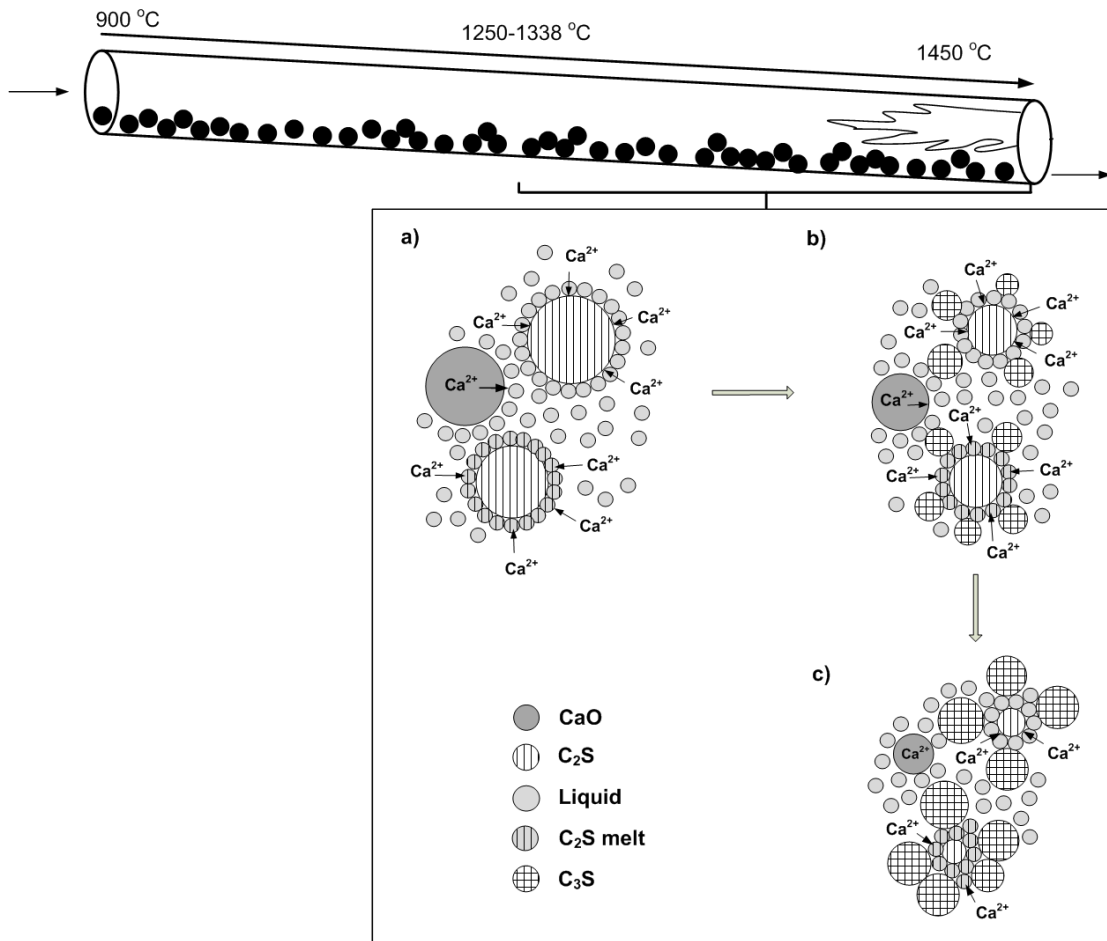


Fig. 2-20: Alite formation. a) Diffusion of Ca²⁺ ions in the direction of belite, which is either crystalline (upper C₂S particle) or partly molten (lower C₂S particle). b) C₃S formation at the interface between the liquid and C₂S particle (upper C₂S particle) and/or in the belite melt phase (lower C₂S particle). c) Growth of alite crystal on the expense of belite.

c) Overview of Clinker Formation in the Industrial Rotary Kiln

The calcined solid material mixture enters the rotary kiln at a temperature of approximately 900 °C. A typical material composition, excluding minor compounds, consists of 64.4 wt.% CaO, 20.1 wt.% SiO₂, 6.3 wt.% Al₂O₃ and 2.4 wt.% Fe₂O₃. At first, the low temperature clinker phases tricalcium aluminate and calcium aluminoferrite (Fig. 2-21b) are formed simultaneously, and belite formation continues from the first formation in the pre-calciner (Fig. 2-21a). These reactions are mainly solid state reactions. A

product layer of fine, packed belite crystals is formed at the interface of CaO and SiO₂ (Fig. 2-23a)). Belite crystal formation and growth occurs in the direction to the SiO₂ particle, as a result of Ca²⁺ diffusion into the first crystal layers of the SiO₂ particles. The aluminate phase is formed by the reaction of CaO and Al₂O₃ (Fig. 2-21b). Ca²⁺ diffuses in the direction of Al₂O particles forming aluminate phase crystals at the interface of the reactant particles. The formation often occurs via the intermediate phase C₁₂A₇. At approximately 1050-1200 °C, Fe³⁺ ions diffuse into previously formed aluminate phase crystals, partly replacing Al³⁺ ion in the crystal lattice and forming the ferrite phase. At this point, both reactions, the aluminate and ferrite phase formation, occur simultaneously. The concentration of formed belite, aluminate and ferrite reaches a maximum at around 1250 °C. Melt formation (circa 15-20 wt.%) occurs at temperatures between 1250 and 1338 °C after which the aluminate and ferrite phase, remaining SiO₂ and/or belite then melt (Fig. 2-21c). The liquid phase accelerates all further clinker formation reactions and prevents the formation of clinker dust due to the formation strong agglomerates (Fig. 2-21d). The formation of alite occurs at temperatures greater than 1250 °C either by solid-liquid reactions, liquid phase reactions or both (Fig. 2-21e). CaO dissolves partly in the melt, and Ca²⁺ ions diffuse in the direction of the belite product, where the formation reaction occurs. Subsequently, either, the belite phase is molten and alite crystallizes out of the melt (liquid phase reactions) or the solid belite is converted into alite by Ca²⁺ penetration into the defect sides of the solid belite (solid-liquid reaction).

The hot clinker exits the kiln and is cooled rapidly to a temperature below 1250 °C to prevent the decomposition of alite to belite and CaO. The final clinker product consists of about 50-70 wt.% alite, 15-30 wt.% belite, 5-10 wt.% aluminate and 5-15 wt.% ferrite phase.⁷

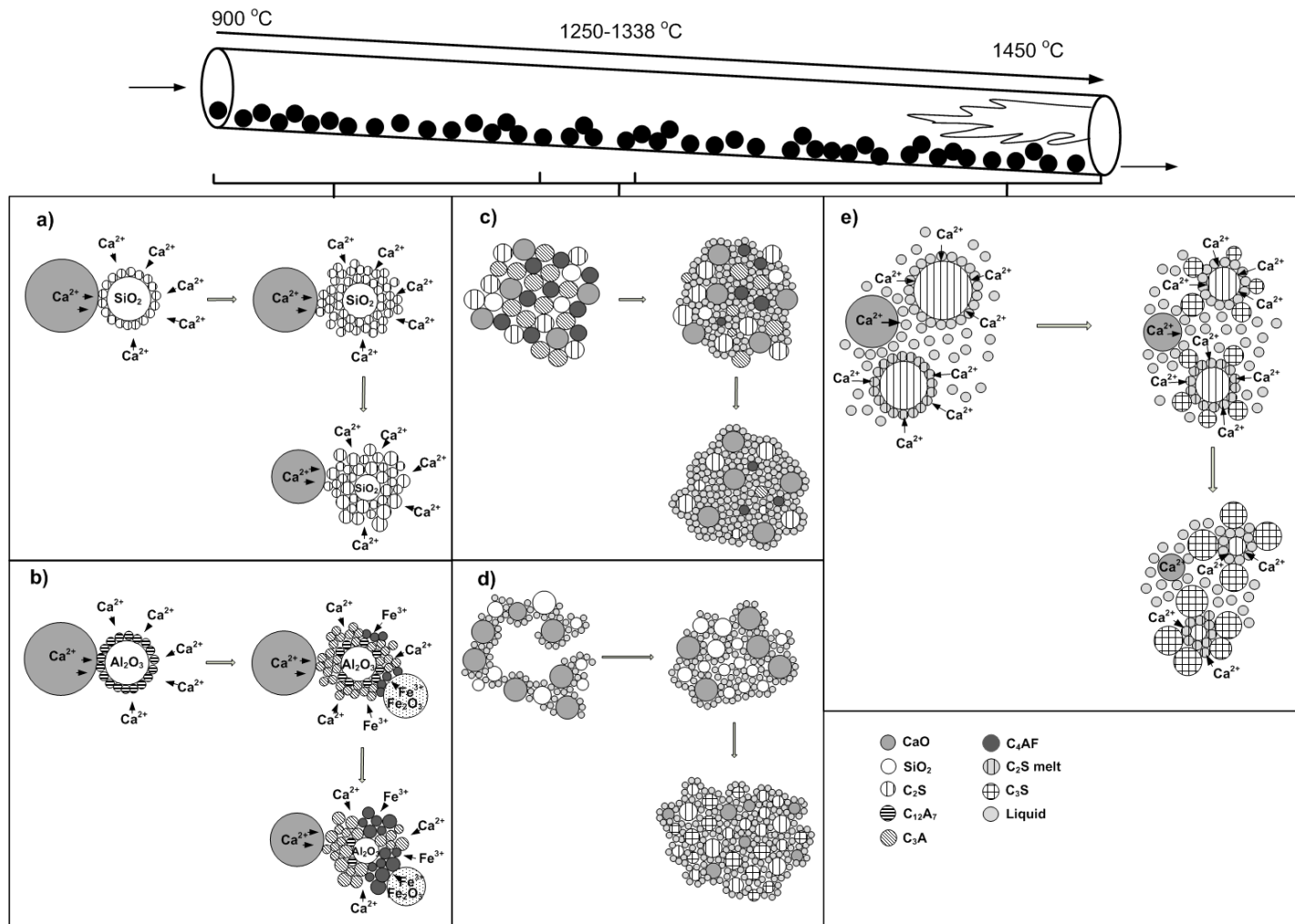


Fig. 2-21: An overview of clinker phase formation in an industrial rotary kiln. a) the formation of belite; b) the formation of the aluminate and ferrite phase; c) the melt formation; d) the formation of agglomerates; e) the formation of alite.

2.4.3 Influence of Raw Material Particle Size Distributions

The fineness of raw materials is an essential factor in the quality of the clinker/cement product, and therefore requires careful treatment in order to carry out cement production in an economically efficient way. As a rule of thumb, with finer raw material particles, the burnability of the raw meal improves, which allows clinker burning at lower temperatures and/or at shorter retention times.^{27,28} Actually, particle fineness affects the homogeneity of the product, clinker crystal sizes and the conversion degree of the reacting compounds. Coarse particle sizes cause inhomogeneities in cement raw meal, resulting in local volumes with chemical compositions deviating from the average composition. Therefore, the particle sizes of pure raw materials such as limestone and sand are of more crucial influence than other mixed raw materials such as marl, which feature certain homogeneity of their own. In general, particle size effects are discussed in the literature only in connection with the calcareous and siliceous compounds of the raw meal, but not for the Al_2O_3 and Fe_2O_3 compounds. The latter two compounds are added mostly to the cement raw meal in the form of mixed raw materials and are therefore relatively fine and uniformly distributed.

The following discussions about the influence of particle sizes and size distributions are based on the assumption of a constant overall chemical composition of raw meals. Differences exist only due to variations in particle size fractions. For a better understanding, raw meal compositions with an overall LSF of 100% are assumed, so that theoretically all CaO in the raw meal is consumed completely for the formation of the clinker phases.

The influence of coarse particles on clinker properties has been qualitatively described by Johansen^{26,28} utilizing the $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$ phase diagram at 1500 °C (Fig. 2-22). This phase diagram shows several areas of interest:

- two-phase areas (A1, A3 and A5) and three-phase areas (A2 and A4)
- area A1 denotes all compositions of CaO in equilibrium with the melt of any composition on the isotherm between points M1 and M2.
- A3 area indicates compositions of alite in equilibrium with the melt of M2-M3,
- in area A5 belite is in equilibrium with melt of M3-M4

- the three-phase area A2 marks all compositions of CaO and alite in equilibrium with the melt of composition M2
- in area A4 alite and belite are in equilibrium with the melt of M3 composition.

The following discussion should be understood as an example of one out of many possible raw meal compositions and is not claimed to be complete.

As a starting condition for the following discussion, a typical cement raw meal composition, denoted by point P in area A4, will be assumed. It can be understood as an average or overall raw meal composition with an LSF of 100%.³⁴ Due to inhomogeneities, caused by coarse particles and by poor blending, the raw meal also contains areas (local volumes) represented by oxide compositions (CaO, SiO₂, Al₂O₃) related to the A2 and A5 areas, which are characterized by LSF's different from the average LSF: higher than the average LSF in area A2 (161%) and lower than the average LSF in area A5 (e.g. 66%).³⁴ It is assumed, that the concentration of Al₂O₃ and Fe₂O₃ are constant, the local volumes differ only in [CaO] and [SiO₂].

The starting conditions are shown in Fig. 2-23a). The figure in the center represents the average raw meal composition of finely ground, homogeneously mixed CaO and SiO₂ particles (A4). For the sake of simplification other compounds such as Al₂O₃ are considered present only in the melt phase. The picture on the left side shows the case of coarse SiO₂ particles characterized by area A5 and the picture on the right side indicates compositions containing coarse CaO particles as in area A2. Both areas are in contact with A4. It should be borne in mind that the starting condition is not represented by the phase diagram of Fig. 2-22, since only the oxides and no reaction products or melt are present. Further discussions deal with the case of isothermal heating at 1500 °C, but qualitatively they are also valid for non-isothermal heating from temperatures above 1338 °C, where the occurrence of a melt phase sets in. Heating the raw meal results in clinkerization reactions within the local volumes, reaching local equilibrium.^{23,26-29} In the case of the raw meal composition of A4 (center figure in Fig. 2-23b), CaO and SiO₂ particles react to form a phase of alite and belite crystals, which is in equilibrium with a melt denoted by point M3 in Fig. 2-22. Coarse SiO₂ particles from area A5 lead to the formation of belite clusters (left picture in Fig. 2-23b). Diffusing Ca²⁺ reacts with the SiO₂ particles resulting in belite crystals roughly twice the size of the former SiO₂

particle.³³ The belite particles are in equilibrium with a melt of a composition situated on the isotherm somewhere between the point M4 and M3 (Fig. 2-22). In contrast, the presence of coarse CaO particles (area A2 in Fig. 2-22) affords free CaO, which has not been consumed for the alite reaction. The free CaO particles are either the remains of former coarse CaO particles or form from melt recrystallized CaO agglomerates.²³ Nevertheless, CaO and alite are in equilibrium with the melt phase, as indicated by M2 (right picture in Fig. 2-23b).

All further reactions can be understood as diffusion controlled reactions between the different local volumes.^{26,28} The melt phase (M3-M4) related to the area A5 is poorer in CaO than the melt phase (M3) of A4. CaO diffusion occurs in the melt phase in the direction of M4 (Fig. 2-22), so alite from phase A4 decomposes, forming belite and CaO, which are dissolved in the melt phase. As a result, the local volume with compositions of area A5 increases (growth of the belite cluster), whereas A4, containing alite and belite, decreases (Fig. 2-23c). On the other hand, the melt phase of the A2 area is rich in CaO (M2), causing diffusion of CaO in the direction of melt phase M3 of A4, where it reacts with belite crystals to form alite (area A3) (right-hand pictures in Fig. 2-23c). Both processes continue with increasing heating time. The formation of alite (A3) stops, when all free CaO has been consumed. Local volumes with a composition of area A2 disappear (right side of Fig. 2-23d). In contrast, the dissolution and diffusion of CaO from decomposed alite in area A4 only stops, when the melt phase composition of area A5 has reached M3 (left side of Fig. 2-23d). In this case, all A4 alite has been decomposed and A4 degenerated to a boundary layer between A5 and A3.

The formation of the clinker phases is a diffusion controlled process and therefore final product composition is strongly dependent on temperature and time. For any raw meal of a composition of LSF less than or equal to 100% a complete reaction of CaO with other raw meal compounds to form the clinker phases, irregardless of the degree of inhomogeneity due to coarse particle size, is theoretically possible, if adequate reaction times and maximum temperatures (excluding the case of total melt formation) are chosen. Higher temperatures increase the amount of CaO dissolving in the melt, as well as the diffusion of Ca^{2+} , while longer reaction times allow diffusion of the different compounds,

especially Ca^{2+} , even over long distances ($> 0.3 \text{ mm}$)³⁰ and through tightly packed crystal structures until no more diffusion gradient persists between the local volumes.

Usually, industrial burning times are shorter than indicated by the sketch, resulting in clinker distributions similar to those highlighted in Fig. 2-23c), with both areas dominated by belite clusters, fairly uniform distributed alite and belite areas, and areas with non-reacted CaO within clinker phases. The inhomogeneity of the raw meal due to coarse particle sizes often leads to the development of big belite clusters embedded in a matrix of alite, instead of homogeneous distribution of alite and belite. Belite has a slower hardening behavior than alite during the hydration reaction in the cement product. A homogeneous distribution of belite in cement is required to ensure a uniform hardening of cement,¹⁰³ so inhomogeneous clinker requires more effort in grinding and homogenization after the clinker cooling. Additionally, belite features a higher hardness than all other clinker phases.¹⁰⁴ Clinker granules containing high amounts of big belite clusters are harder to grind than small, uniformly distributed crystals. All in all, the clinker grinding of an inhomogeneous product, as described above, results in higher energy consumption (electrical energy) and wear on the grinding mills. Conversely, if the temperature and/or the retention time of the material in the rotary kiln are increased to allow the conversion of CaO and belite cluster to alite, belite and alite crystals in other more homogeneous local areas will grow in size. Clinker products rich in big alite and belite crystals could cause problems during clinker grinding, even though energy consumption and material wear would be somewhat lower than in the case of high concentrations of belite clusters. Furthermore, the increasing costs of fuel in order to achieve higher maximum temperatures and longer burning times need to be opposed to the costs of the energy consumption of clinker grinding and maintenance of the clinker grinding mill. A third consideration needs to be taken into account owing to the fact that a small concentration of free CaO ($\leq 2 \text{ wt.}\%$) in the final clinker is acceptable and potential higher concentrations can be counteracted by reducing the CaCO_3 concentration in the raw meal. Of course, this would not affect the possible formation of belite nests in the case of coarse siliceous particles. All of these considerations show, how complex the correlation between the chemical and physical composition of raw meal is and how

careful adequate process steps need to be considered, i.e. raw material grinding cost vs. fuel costs vs. electrical energy and maintenance costs.

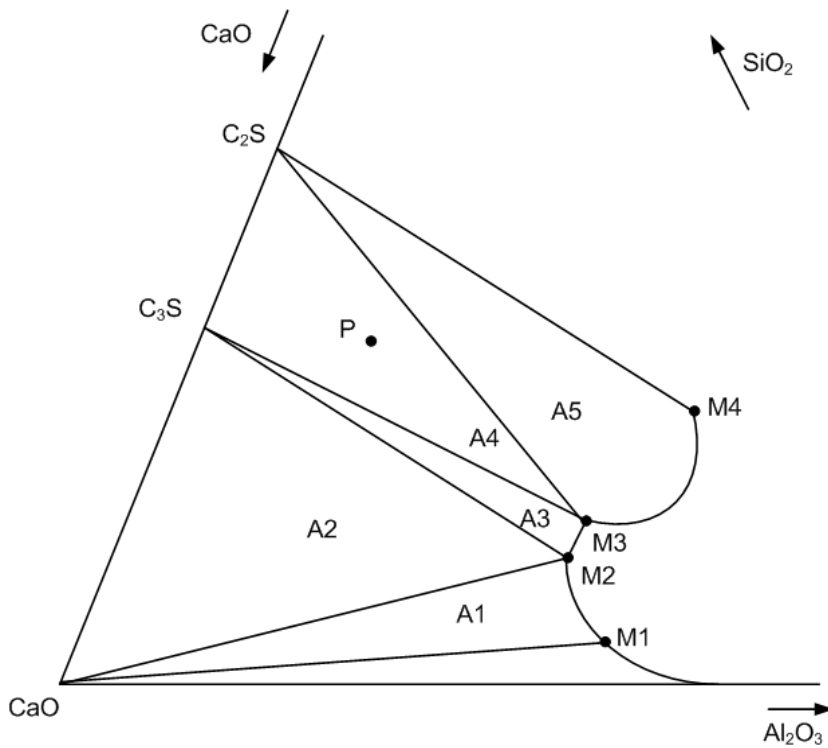


Fig. 2-22: The part of the ternary phase diagram CaO-SiO₂-Al₂O₃ relevant for compositions typical for Portland cement clinker showing the composition of different areas. A1: compositions of CaO in equilibrium with the melt of any composition M1-M2; A2 compositions of CaO and C₃S in equilibrium with the melt of M2; A3 compositions of C₃S in equilibrium with the melts of any composition M2-M3; A4: compositions of C₃S and C₂S in equilibrium with the melt of M3; A5: compositions of C₂S in equilibrium with the melt of any M3-M4 composition.²⁶

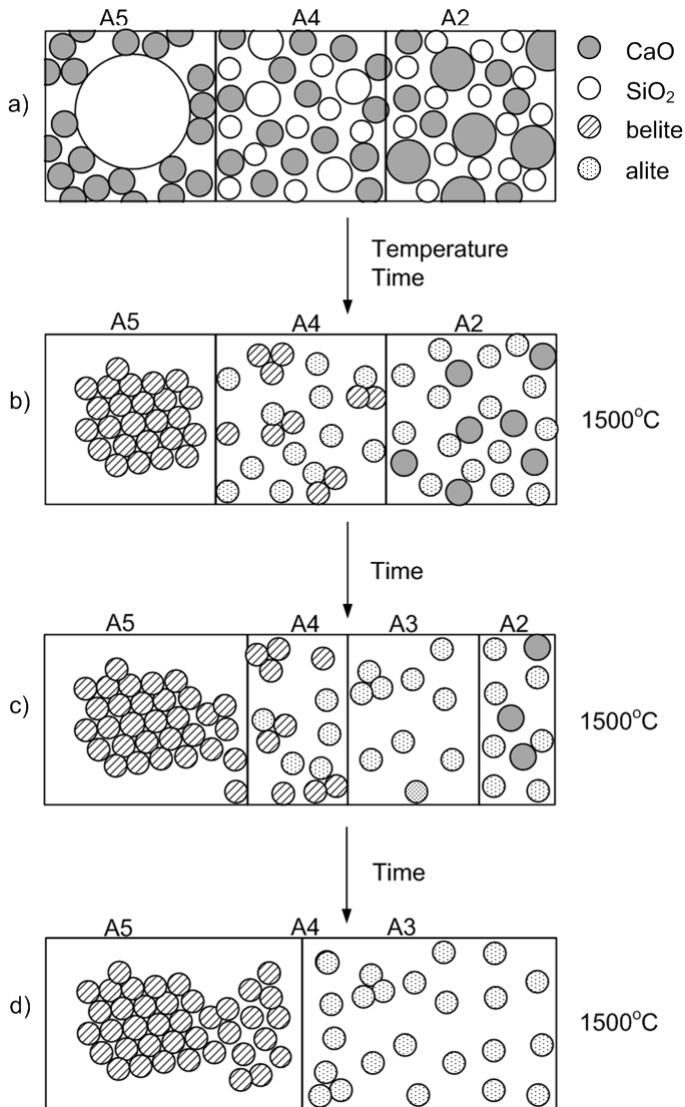


Fig. 2-23: The formation of alite and belite depending on the particle size of CaO and SiO₂ particles. a) A5: Coarse SiO₂ particles are surrounded by fine CaO particles; A4: finely ground, homogenously mixed CaO and SiO₂ particles; A2: Coarse CaO particles surrounded by fine SiO₂ particles. b) Formation of belite and alite; A5: formation of the belite cluster; A4 belite and alite are homogenously distributed; A2: formation of alite and free CaO is left; c) A4: Diffusion of CaO into the melt and decomposing of alite; (A5) the belite clusters grow in size due to the decomposition of alite (A4); A2: Diffusion of CaO in the direction of the belite phase of A4, forming alite (A3). d) Continuing growth of belite clusters (A5) and distributed alite crystals (A3) until belite (A4) is consumed.

The term “particle fineness” refers to particle sizes as well as particle size distributions. Particle size distributions are used, if the burnability of a raw meal is classified, whereas specific particle sizes (diameters) are referred to, when the influence of one compound on clinker formation and product properties is discussed. The influence of particle size distributions on burnability was extensively investigated in laboratory tests by Heilmann.²⁷ As a general tendency it could be concluded, that higher weight fractions of small particles in raw meal result in better burnability. It has been found, that the weight fraction of particles below 0.015 mm should be circa 35 wt.%. In comparison, decreasing the amount of this particle fraction in a raw meal resulted in a significantly lower burnability. On the contrary, an increase in the weight fraction did not improve burnability. For each raw material (CaCO_3 and SiO_2 in different raw materials such as sand, clay, marl, slag and marble) a significant fraction needs to be smaller than 0.05 mm, otherwise burnability is negatively affected. Of course, precise values are not applicable to each industrial raw meal, but the tendencies are. As a matter of fact, as unique raw meals of each works are, as individual is also the optimal particle size distribution of each raw meal. In each case burning tests are required to determine the most suitable particle fineness.²⁷

Critical particle sizes refer to the maximum acceptable particle diameters of the different mineralogical calcareous and siliceous compounds in raw meal to prevent impairment of burnability. Typical (approximate) values for critical particle sizes given in literature are 0.15 mm,²⁷ 0.125 mm,^{23,32,33} 0.09 mm,²⁷ 0.63 mm,³¹ and 0.044 mm^{23,32,33} (although the actual mesh size would be 0.045 mm). They have been obtained through laboratory clinker burning tests at 1400 °C for 30 minutes utilizing ordinary sieves of standard mesh sizes to fractionize the raw meal compounds. The first two values are related to the calcareous compounds in the raw meal, the latter three to the siliceous compounds. The values of the maximum diameter of 0.15 mm and 0.09 mm are based on the extensive studies of Heilmann.²⁷ Both were replaced by other values (0.125, 0.063 and 0.044 mm).^{23,31-33}

Particle sizes of pure calcite larger than 0.125 mm increase the local LSF drastically, for example by $\Delta\text{LSF} \sim 25$ ³⁴ and result in dense non-reacted CaO clusters³⁶ in the clinker

product within normal reaction times (30-45 minutes) and for maximum cement plants burning temperatures. Furthermore, the concentration of the clinker phases, most likely of alite since it is formed in the final step, will be lower than theoretically possible from the overall chemical composition, because less dissolved CaO is available for the formation reaction. Particles of calcareous marl greater than 0.125 mm lead often to clusters of small alite crystals surrounded by non-reacted CaO.³⁶ Small alite crystals are formed due to the natural occurrence of SiO₂ in marl. If a marl particle has a cementitious composition, e.g. LSF=92-98%, SR=2-3% and AR=2-3%, then alite crystals, small amounts of belite and very small amounts of non-reacted CaO are formed.³⁶ Therefore, large calcareous marl particles are problematic, if the chemical composition is somewhat different from normal cementitious compositions. Coarse CaCO₃ particles in the rotary kiln feed are not only a result of poor raw material grinding. Fine CaCO₃ (resulting in dusty CaO due to calcination) causes coarsening of the particle sizes in the kiln feed. Dusty CaO entering the rotary kiln is easily floated by the kiln gases and transported out back to the calciner and pre-heater cyclones. Early liquid formation causes the formation of agglomerates, which are separated from the gases in the cyclone system and enter kiln feed often as particles above the critical size (up to 1 mm).³⁵

Adjusting the particle size of siliceous compounds is of more importance than for calcareous compounds, since the results are not only non-reacted CaO clusters and lower concentrations of alite, but also dense belite clusters that cause numerous down-stream problems like poor grindability. Most crucial are quartz, flint and slag particles greater than 0.044 mm.^{31,36} Here, large belite crystals (~ 0.6 mm,^{31,36} in the modern kiln systems ~0.2 mm¹¹⁷) are formed and compacted in densely packed belite clusters, often with an acid insoluble siliceous core (for particle greater than 0.2 mm).^{31,36} Particles of other siliceous materials such as marl, shale and feldspar (low in CaCO₃ concentration) should exist in the raw meal as particles less than 0.063 mm, otherwise irregular belite clusters with crystals of 0.3-0.4 mm are formed. The undesired effect of belite clusters on clinker quality has been described previously.

An overview of the effect of specific mineralogical compound particles exceeding the critical diameter on the final clinker product is given in Tab. 2-4.^{31,36}

Tab. 2-4 The effect of particle sizes of different mineralogical compounds in raw meal on the clinker product.^{31,36}

Raw meal compound	Critical particle size	Effect on clinker product
Coarse quartz, flint, slag	> 0.044 mm	• compact, spherical shaped belite clusters with large belite crystals and very low amount of interstitial melt • “insoluble” siliceous core • clusters often surrounded by large alite crystals • non-reacted CaO • incomplete alite formation
Marl, shale and feldspar low in CaCO_3 concentration	> 0.063 mm	• irregular-shaped belite cluster with a considerable amount of interstitial melt • non-reacted CaO • incomplete alite formation
Pure calcite	> 0.125 mm	• dense clusters of non-reacted CaO • incomplete alite formation
Calcareous marl	> 0.125 mm	• clusters of small alite crystals surrounded by non-reacted CaO • small amounts of interstitial melt between alite crystals

2.5 Future work

State-of-the-art clinker formation in a modern rotary kiln consumes high levels of energy and therefore causes high costs related to high fuel consumption. Great effort has been put into reducing fuel costs by replacing fossil fuels with cheaper alternative fuels. It should, however, not be forgotten that a higher demand for alternative fuels will likely also result in higher costs for these alternative fuels. An effective reduction of costs in the future will probably only be achieved by the reduction of consumed energy, especially thermal energy. This will require a radical change in how technology is utilized for cement production and/or the development of a novel low energy cement product. Both options require a fundamental understanding of the different clinker formation processes. Despite long and intensive research on the topic, a lack of knowledge on some basic mechanisms in clinker formation still exists. The development and behavior of individual clinker phases have been shown to depend on reactant concentrations, burning temperature and burning time. In separately performed (i.e. not under clinker burning conditions) rotation tests with solids and liquids (often sand and water) knowledge about granulation and agglomeration has been gained. In order to understand reaction mechanisms in an industrial rotary kiln, investigations should not only be carried out with preformed granules, but also in laboratory-scale rotary kilns, which actually combine clinker formation and granulation both of which take place simultaneously in an industrial rotary kiln. A first attempt was carried out by Maas *et al.*³⁷, but more detailed investigations are still necessary in order to correlate laboratory and industrial-scale investigations. The most relevant issue for cement plant operation is an investigation of melt formation in the reactor. As described above, melt formation influences the granulation of solid materials, establishing close contact between the particles and thereby accelerating clinker formation. Since little is known concerning the first formation of melt for a specific raw meal, the starting formation of agglomerates, depending on the temperature and thus on the location in the reactor, cannot be predicted. While these phases usually are formed via solid-solid reactions in laboratory experiments given sufficient reaction time, it might not be the case in a rotary kiln. Assuming the formation of melt occurs above 1250 °C,¹⁶ implies that the feed material exists mainly as a loose powder mixture at lower temperatures in the rotary kiln. In this case, the primary

requirement for solid state reactions, i.e. high material contact, is not necessarily met, which can lead to significant discrepancies between laboratory studies and industrial applications. As an example, the formation of belite ($\sim 50\text{wt.}\%^{37}$) has already been reported at $1000\text{ }^{\circ}\text{C}$ in a laboratory study. However, since no close contact between the raw meal particles has been established at these low temperatures in a rotary kiln, significantly lower amounts of belite will form under industrial conditions. It is possible, though, that melt formation starts already at lower temperatures due to minor compounds and local inhomogeneities, causing early agglomeration and solid-liquid phase formation even for the belite, aluminate and ferrite phases. Whether this is the case and if early melt formation is beneficial on an industrial level, should be the subject of further investigations and might also be exploited in future applications.

Furthermore, a better understanding of particle-particle and particle-melt interactions in connection with clinker formations is vital. The formation of clinker phases occurs at the interface between two solids or a solid and a melt. Therefore, the contact area has a direct influence on the formation rate of the crystal phases. In a rotary kiln the contact area between particles is rather high, depending on factors such as particle sizes/size distributions and material fill height (hence pressure on the reacting material caused by the material load). The influence of individual parameters needs to be understood in a more quantitative way, as it is of great importance, especially for investigating and developing future clinker burning technologies and new cement products.

2.6 Conclusions

In this paper an introduction to the extensive field of cement was given and the literature on clinker crystal phase formation at temperatures between 900 and $1500\text{ }^{\circ}\text{C}$ was summarized. Special focus was laid on the step-wise mechanistic formation of the four major clinker phases under laboratory conditions. Based on these investigations a clinker formation mechanism in an industrial rotary kiln was outlined. The most important findings are:

- clinker phase formation occurs via solid state, solid-liquid and/or liquid-liquid reactions

- in raw meal consisting only of the four major oxides CaO , SiO_2 , Al_2O_3 and Fe_2O_3 , belite, aluminate and ferrite are formed by solid state reactions, while alite is formed mainly by solid-liquid and/or liquid-liquid reactions
- a melt phase is formed at 1338 °C in absolutely homogenous raw meal
- inhomogeneities and additional oxides (minor and trace compounds) decrease the temperature at which melt formation sets in
- the formation of the alite, belite and the aluminate phases occurs due to the diffusion of Ca^{2+} as it is the species with the highest mobility through the interface between particles or particles and melt reacting either with SiO_2 or Al_2O_3 particles or the melt
- the ferrite phase is formed by diffusing Fe^{3+} into previously formed C_3A on the expanse of C_3A
- alite is formed by the reaction of previously formed belite with free CaO . There is no consensus in the literature, as to belite melts or remains crystalline, thus alite formation may take place in the melt phase or at the interface between a melt and the C_2S particles
- particle size and particle size distribution influence clinker quality and the required reaction time/ burnability

Understanding the formation of clinker within a rotary kiln is a crucial prerequisite in optimizing the industrial process. Future laboratory studies should mimic the industrial process more carefully, taking as an example kiln rotation into account. With this review it is hoped that researchers new to the field and aiming for a more fundamental understanding of the process, as well as optimizing this high-impact industrial process, find a simple access point for understanding the basic underlying principles involved in cement production, resulting in future process innovations.

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Chapter 3

Experimental Setup

3.1 Introduction

Full-scale measurement campaigns and investigations at cement plants are very difficult, expensive and not in the interest of the plant manufacture, since the cement production would be interrupted. Furthermore, as mentioned earlier, material sampling and various other measurements (temperature, gas composition) at different locations along an industrial cement rotary kiln (ICRK) may prove to be very difficult. Therefore, a laboratory-scale rotary kiln was designed and built within this project based on a previous study ¹. This new setup, a rotary kiln simulator (RKS), (Fig. 3-1) consists basically of two main parts i.e. an ordinary horizontal heating furnace and a sample motion system and will be described in details below.

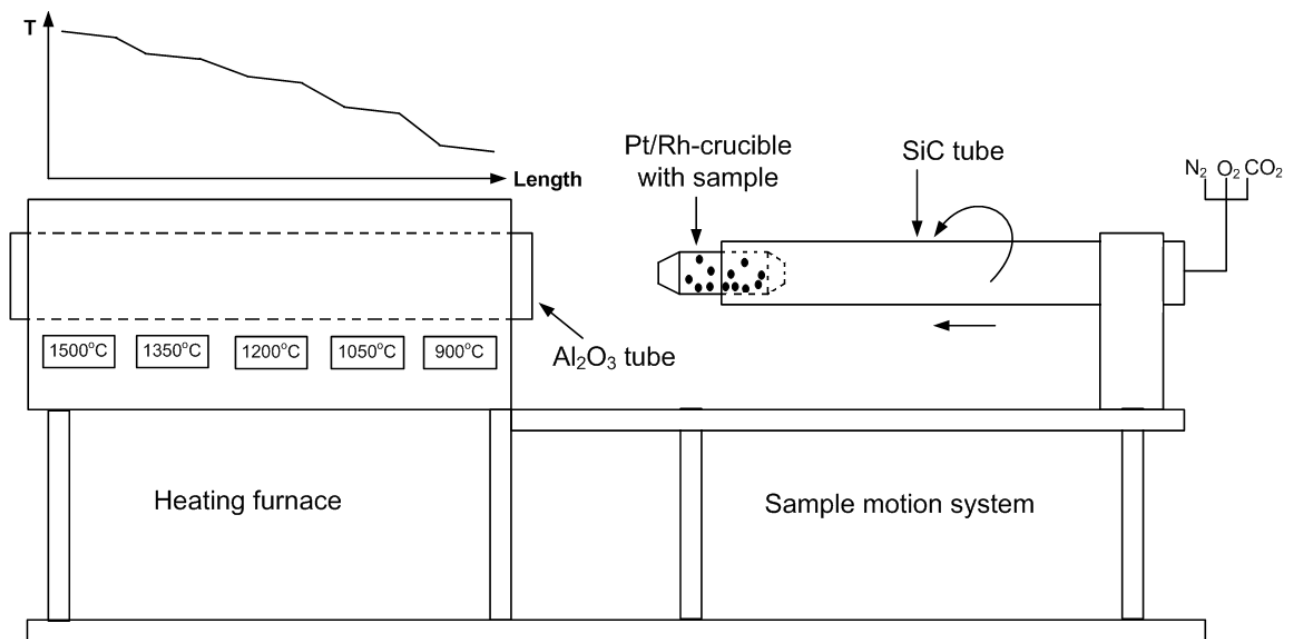


Fig. 3-1: A sketch of the clinker burning lab-scale test-facility. The heating furnace on the left side has 5 heating zones which are set to temperatures between 900 and 1550 °C. The motion part on the right side consists of a SiC tube, in which the sample holder is inserted. The rotating SiC tube is pushed into the heating furnaces with a defined velocity.

3.2 Horizontal Heating Furnace

The heating of the raw material mixtures is provided by a custom-made horizontal heating furnace obtained from Entech Energiteknik AB. The key data of the heating furnace are listed in Tab. 3-1.

Tab. 3-1 Key data of lab-scale heating furnace.

Company:	Entech Energiteknik AB, Ängelholm, Sweden	
Product specifications:	Furnace:	High temperature furnace ETF 100/16-V
	Controller:	Eurotherm 3216
Date of purchase:	July 2009	
Dimensions:	Length:	1222 mm
	Width:	530 mm
	Height:	1385 mm
Number of individual heating zones:	5	
Length of each heating zone:	180 mm	
Heating elements:	MoSi ₂	
Heating principle:	Resistance heating	
Temperature limit:	1800 °C	
Ceramic tube material:	Sillimantin 60:	Type C530 (DIN EN 60672) 72-74 % Al ₂ O ₃
	Sillimantin 60NG:	72-74 % Al ₂ O ₃
Tube dimensions:	Length:	1300 mm
	Inner diameter:	75 mm
	Outer diameter:	85mm

The horizontal heating furnace has five individually adjustable heating zones (Fig. 3-2, HZ1-HZ5), each of a length of 180 mm. They are heated by MoSi₂ type heating elements, which are protected by a ceramic alumina tube through the center of the furnace (Fig. 3-1). All heating zones are

controlled from a PC. In the usual operating mode the heating zones are set to create temperature gradients mainly between 900 and 1550 °C in order to simulate temperature profiles, which are expected to occur in an industrial reactor.

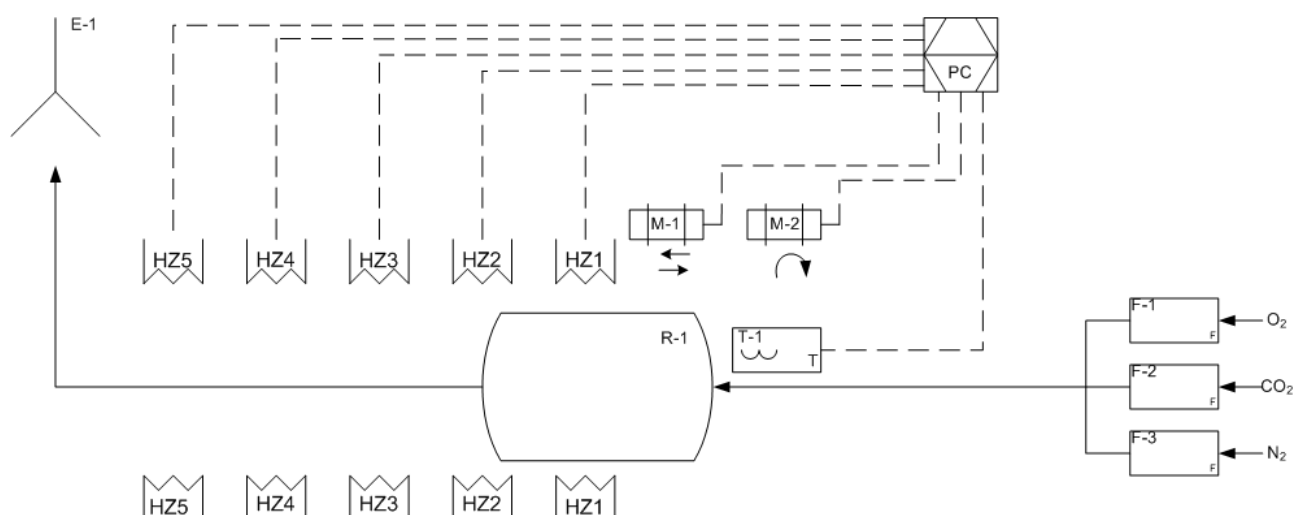


Fig. 3-2: The PI diagram of the setup. HZ1-HZ5 are the 5 individual heating zones. M-1 and M-2 are the step-motors for the horizontal motion and for the rotation of the SiC tube, respectively. F-1 – F3 are the gas flow meters for oxygen (O₂), carbon dioxide (CO₂) and nitrogen (N₂). Released gas exits to the exhaust E1. The temperature inside the SiC tube is measured by an S-type thermocouple (T-1) behind the platinum crucible (R-1). The temperature of the heating zones and the motors are PC-controlled by Lab view software (PC); the measured temperature (T-1) is logged.

3.3 Sample Motion System

The movement of the solid material through the industrial rotary kiln occurs due to a tilted positioning and the rotation of the reactor. This is simulated with the sample motion system of the setup.

The sample motion system (Tab. 3-2) consists mainly of a ceramic SiC tube, which is connected to two step motors. One of the motors is moving the ceramic tube along the horizontal axis into the alumina tube of the heating furnace. The second step motor rotates the tube around its horizontal axis. Both motions are adjustable with respect to the velocity and are controlled by a PC. The velocity of the SiC tube through the furnace can be changed five times during one heating program cycle. This enables adjustments with respect to differences in the steepness of the temperature

gradient along the heating furnace to obtain better control over heating rates (for more details see section 3.5).

The raw meal sample, held by a platinum crucible, is placed into the SiC tube at the end facing the heating furnace. Platinum reacts with silicon carbide (SiC) forming various Si-Pt alloys ², which requires the protection of the expensive platinum crucible by coating the end (ca. 120 mm) with an Al₂O₃ engobe, which must be replaced frequently. Therefore, the SiC tube end is dipped into the liquid Al₂O₃ engobe-suspension. It is important to coat only the minimum required area for the Pt/Rh-crucible protection, since the coating promotes the formation of glass from SiC, significantly decreasing the lifetime of the SiC tube. After drying, the coating was burned at 1200 °C for 2 h, which turned the engobe into a hard ceramic coating. The coating needs to be replaced, when too much glass melt has been formed inside the SiC tube increasing the risk of getting the Pt/Rh-crucible stuck. The use of an alumina tube instead of a SiC tube was not possible, since alumina is prone to thermal shock and fast heating and cooling, as it is utilized for the clinker burning experiments, will result in tube breakage.

At the opposite end to the coated end, gas or gas mixtures (N₂, O₂ and/or CO₂) can be introduced into the SiC tube.

Tab. 3-2 Key data of the sample motion system.

Step motors:	
Tube material:	SiC, partly coated with Al ₂ O ₃
Tube dimensions	Length: 1800 mm Inner diameter: 48 mm Outer diameter: 60 mm
Software:	Lab-View
Pushing velocity:	0.1-65 mm/s
Drag speed:	33 mm/s
Rotation velocity:	0-28 rpm
Feed gases:	CO ₂ , N ₂ , O ₂
Gas flow:	2.2 L/min
Thermocouple:	S-type; Pt-Pt/Rh wire in alumina rod

3.4 Platinum Crucible

The raw meal for clinker formation needs to be placed into a sample holder (reactor) of inert material. Cement/clinker raw materials consist mainly of CaO , SiO_2 , Al_2O_3 and Fe_2O_3 , which react with most ceramic materials at high temperatures³. Therefore, ordinary alumina crucibles cannot be used and a special Pt/Rh-crucible was designed (Tab. 3-3).

Tab. 3-3 Key data of the Pt/Rh-crucible.

Material:	90 % platinum; 10 % rhodium	
Main body dimensions:	Length:	85 mm / 95 mm
	Inner diameter:	43 mm
	Outer diameter:	43.5 mm
Gas inlet:	Opening:	15 mm
	Inner cone opening:	5-15mm
	Inner cone length:	10 mm
Lid:	Length:	25.5 mm
	Inner diameter:	45.8 mm
	Outer diameter:	46.6 mm
	Gas outlet $\varnothing$:	10 mm

The material of choice, also rather expensive, is platinum. Here, an alloy of 90% platinum and 10 % rhodium was used for the specially designed crucible. The crucible consists of a cylindrical main body and a conical lid (Fig. 3-3). The lid is mounted to the main body by three pins. Both ends of the crucible have openings to ensure a sufficient gas flow through the reactor. The gas entrance opening is specially designed to ensure a well- distributed gas flow through the reactor. An inner cone is attached to the opening, which channels the gas flow along the platinum wall and through the center of the crucible (Fig. 3-3 and Fig. 3-4). Nitrogen, oxygen and CO_2 are utilized to simulate different atmospheres inside the crucible. About 80 % of the main body is placed into the SiC tube of the pushing system (Fig. 3-4). The lid part is outside of the tube. The crucible can hold a maximum ca. 25-30 g raw meal, which corresponds to a fill height of ~30 %. The level of the

maximum fill height is right below the gas openings, in order to minimize on one hand the loss of material and maximize the usage of the crucible to burn as much material as possible at once.

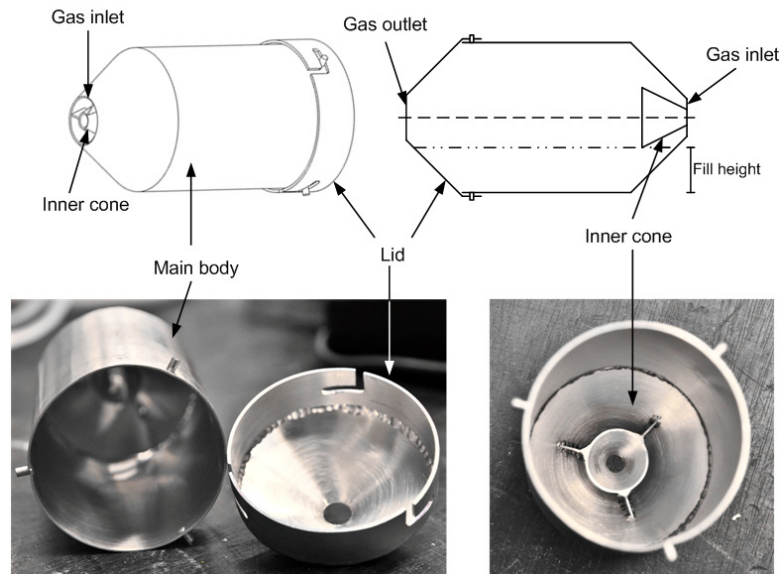


Fig. 3-3: A sketch of the platinum crucible. It consists of a main body and a lid to easily insert and take out the sample. The main body is inserted into the ceramic tube of the pushing system. To ensure sufficient gas flow, the gas inlet contains an inner cone to distribute gas along the crucible wall and the center.

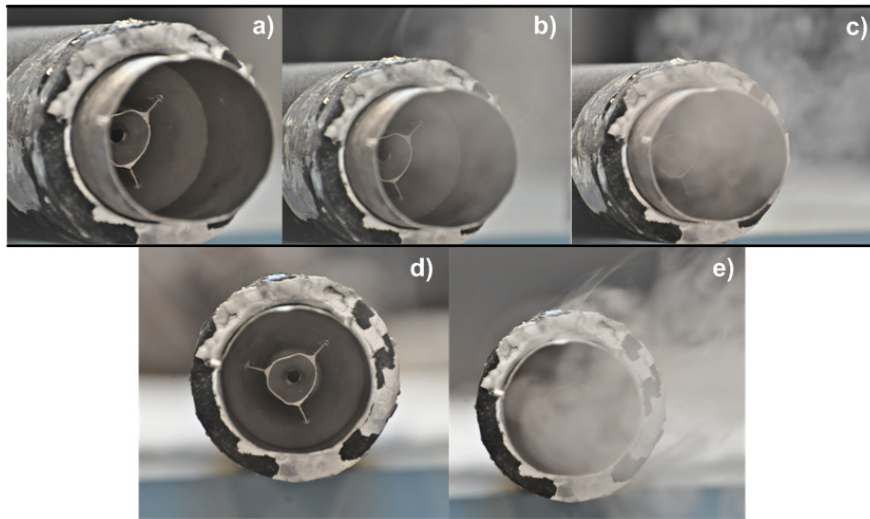


Fig. 3-4: The platinum crucible inserted into the ceramic tube of the motion system. Smoke was used to visualize the gas flow through Pt/Rh-crucible (pictures a-e). In the side view (a) and front view (d) the special gas entrance is visible, through which the smoke distributes into the whole Pt/Rh-crucible show the flow of smoke (b, c and e).

3.5 Comparison of RKS and ICRK

The RKS was built to simulate clinker formation processes as they might occur in ICRK's. The most important characteristics of an industrial kiln are implemented in the new setup: non-isothermal heating and the rotational motion. In order to construct a setup, which is simple to operate and with reasonable control over all important parameters (e.g. temperature, heating rate) at reasonable cost, a design was chosen still having differences from the industrial cement rotary kiln. These differences are listed in Tab. 3-4.

Tab. 3-4 Comparison of design features of the RKS and the industrial cement rotary kiln.

RKS	Industrial cement rotary kiln
• Batch process • Heating from the outside, by resistance heating • Even bed material temperature • Smooth walls and inert material for sample holding (Pt/Rh-crucible) • Co-current gas flow • “clean”, controlled gas atmosphere	• Continuous process • Heating from the inside, by fuel combustion • Temperature gradient in bed material due to bed height • Refractories of ceramic material • Counter-current gas flow • Circulation of material and volatiles

a) Batch vs. Continuous Process

For most general clinker formation experiments the batch mode is most suitable and preferred, since it allows control over experimental parameters and stepwise clinker formation investigations (time- and temperature wise). In the following an example of the advantage of the batch process compared to the continuous process is discussed. One of the most important parameters, which needs to be controlled, is chemical composition. In a batch process the growth of inhomogenous lining/rings on the reactor walls (as it would occur in the continuous process) is avoided. Thereby, mixing of matter with different compositions is avoided, which could change the chemical composition of the bed material compared to the raw meal feed ⁴.

b) Direction of Heat Transfer and Temperature Distribution in the Bed

A vital difference of the setup compared to the industrial process is the direction of the heat transfer. In the ICRK the heat is applied from the inside by the combustion of fuels (cf. Fig. 2-4). In the RKS the heat is supplied from the outside of the Pt/Rh-crucible by electrical resistance heating. As a rough description a temperature gradient occurs from the center towards the reactor wall in the industrial process and vice versa in the new simulator setup. The industrial process is characterized by complex heat transfer phenomena (Fig. 3-5a). Since, the amount of sample clinkerized in the RKS during one experiment is small (ca. 15-20 g), it is a fair assumption, that the vertical temperature gradient in the RKS is only minor, in contradiction to the industrial process, simplifying the description of the heat transfer significantly (Fig. 3-5b). In the industrial process, the temperatures of the bed surfaces towards the gas atmosphere and the reactor wall are higher than in the core of the bed. These temperature differences can be simulated by temperature dependent clinker formation test series in the lab-scale setup.

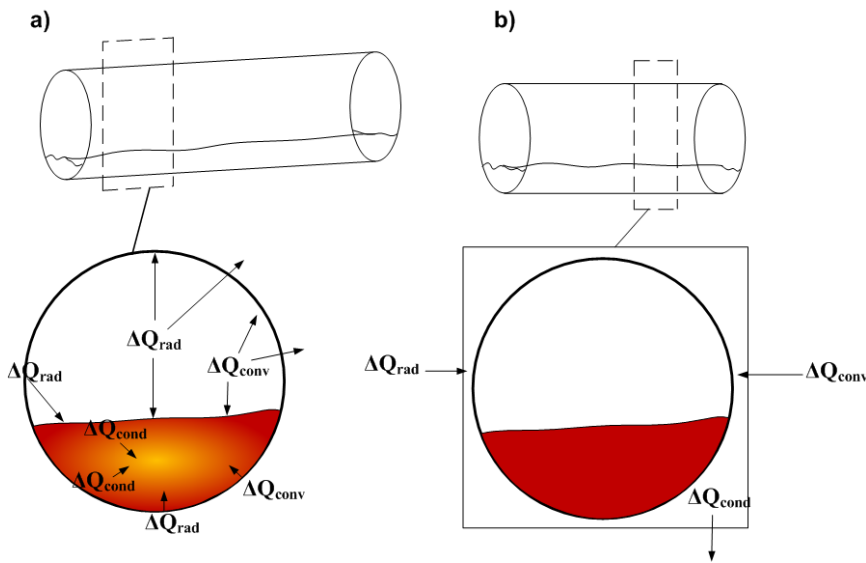


Fig. 3-5: Heat exchange in a) an industrial cement rotary kiln and b) the rotary kiln simulator. a) In the ICRK heat exchange occurs between the kiln gas atmosphere, the kiln wall and the bed material by radiation (ΔQ_{rad}), convection (ΔQ_{conv}) and conduction (ΔQ_{cond}). Within the bed material heat is exchanged by conduction in direction to the inner core. b) In the RKS the temperature of the reactor, the gas atmosphere and the bed material are assumed to be equal at a specific furnace cross section. Heat transfer occurs by radiation and conduction from the furnace gas atmosphere to the Pt/Rh-crucible walls. Heat is lost by conduction through the reactor wall to the cross section of lower temperature.

c) Material and Surface Texture of “Reactor” Inner Walls

The inside of an ICRK is covered with bricks to protect the steel shell of the kiln. Over time, lining of material from the bed builds up on the brick, which is especially important as a protective layer at the hot end of the kiln. Both the bricks and the lining function as a rough surface, on which the bed material is rolling. The surface walls in the RKS are very smooth and the Pt/Rh-material is considered to be inert towards the bed material, which is important to ensure control over the chemical composition of the non-volatile part of the raw meal. In contrast, ceramic materials would react with the raw meal/clinker during high temperature experiments. The smooth surface of the Pt/Rh-crucible could limit the rolling motion of the bed material especially at lower temperatures, when no material is stuck on the inner walls because of too low melt formation. Pretests with smooth and roughened glass crucibles at room temperature showed that rough surfaces are required in order to ensure the material is rolling. Thus, the inner walls of the Pt/Rh crucible were roughened with sand paper before the experiments.

d) Gas Flow Direction

Primary and secondary air entering at the lower end of the industrial rotary kiln is heated in the flame area up to 1800-2000 °C ⁵. The counter-current flow of the gas towards to upper end of the rotary kiln heats up the kiln walls and the bed material. The gas exits the kiln at ca. 900 °C. For practical reasons, the gas flow in the RKS is co-current, i.e. it enters the reactor at the colder end and is heated up together with the bed materials as the crucible is moved through the heating furnace. With the low flow rates (2.2 L/min) the gas flow had no significant influence on relevant temperature profiles.

e) Gas Atmosphere Composition

The gas atmosphere in the RKS was simulated by mixing N₂ (~75 %) and O₂ (~25%) to ensure oxidizing conditions during clinkerization reactions. In the gas atmosphere of an ICRK additionally CO₂ and NO_x are present in considerable concentrations as well as alkali sulfates and chlorides evaporating from the bed material. Their evaporation behavior at high temperatures (in the lower end of the kiln) and condensation at lower temperatures (in the higher end of the kiln or preheater) could result in an enrichment of these compounds in the kiln, if no alkali by-pass is installed ⁶. In contrast, these volatiles are removed from the reactor of the RKS by the co-current gas flow thus simulating an ICRK with an alkali bypass.

3.6 Temperature Profiles

The gas and sample temperature inside the Pt/Rh-reactor cannot be measured in the rotational mode. The temperature measurement at temperatures $> 1200\text{ }^{\circ}\text{C}$ are typically carried out using an S-type thermocouple consisting of Pt- and Pt/Rh- wires in a two-hole ceramic Al_2O_3 rod protected by a ceramic Al_2O_3 tube (Fig. 3-6a). The Al_2O_3 rod and tube are fragile at high temperatures due to thermal shock. A tight fixing of the thermocouple inside the SiC tube would be required, to prevent breakage of the thermocouple during setup operation in rotational mode. However, this was not possible and therefore, the furnace gas temperature as well as the sample and the crucible gas and wall temperatures were measured for different furnace temperature settings in non-rotational mode and compared before the clinker burning investigations.

A 1650 mm long S-type thermocouple as described above was used. The ceramic protection at the top end of the thermocouple, where the two wires are welded together (thermocouple tip), is open to ensure a direct measurement of the temperature. The thermocouple was placed inside the SiC tube of the motion system with the top end facing the heating furnace 100 mm before the SiC tube end. This is approximately the furthest point of which the platinum crucible can be inserted into the SiC tube of the motion system (Fig. 3-6b). During an experiment, the temperature at this point is the lowest within the gas atmosphere and material temperature gradient in/of the platinum crucible (Fig. 3-6c). The thermocouple is connected to a temperature controller mounted to the sample motion system. The controller is connected to a computer recording the temperatures.

All temperature measurements have been conducted with a gas flow of 75 % N_2 and 25 % O_2 (2.2 L/min) through the SiC tube.

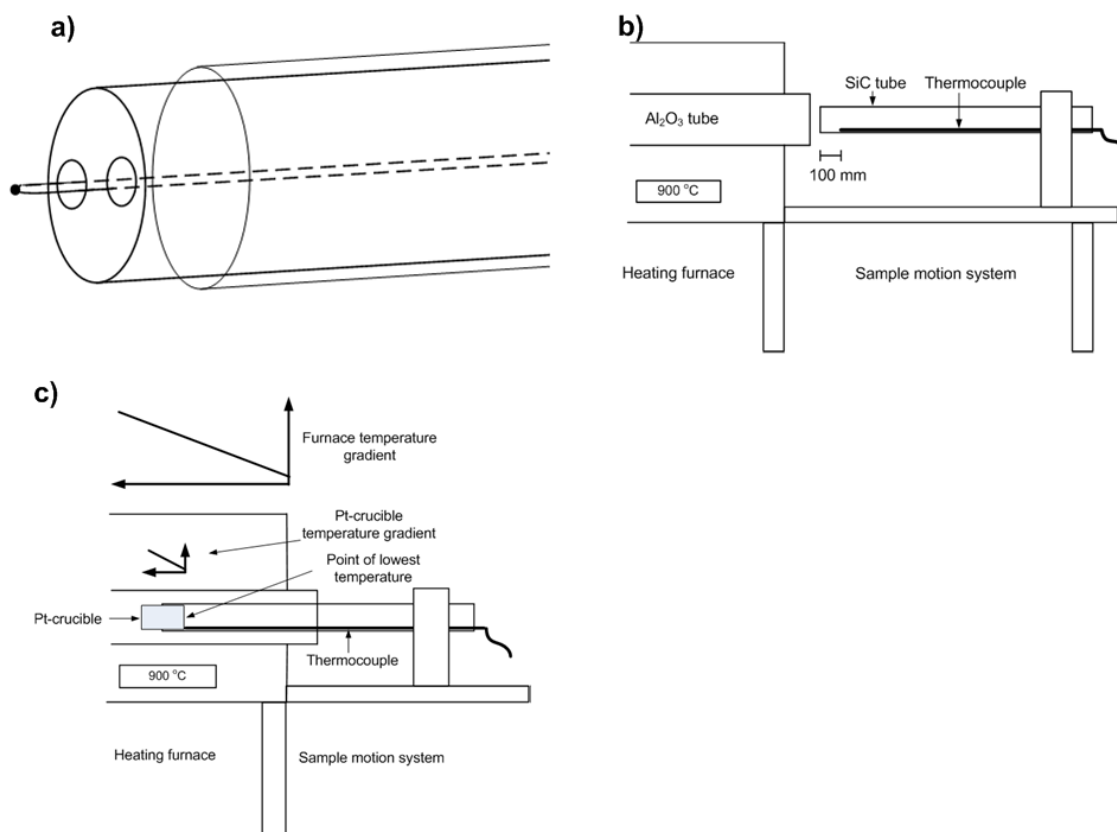


Fig. 3-6: a) The open end of the thermocouple consisting of two wires through an Al_2O_3 rod, welded together at the thermocouple tip. An Al_2O_3 tube is protecting the Al_2O_3 rod. b) Placement of the thermocouple into the SiC tube. The top end is placed ca. 100 mm before the end of the SiC tube facing the heating furnace. c) The theoretical temperature difference along the Pt/Rh-crucible during its movement through the heating furnace.

3.6.1 Gas Temperature Profile in Heating Furnace

Gas temperature profiles in the heating furnace (without Pt/Rh crucible) depending on temperature settings of the heating zones were measured, by moving the SiC tube with the inserted thermocouple stepwise through the furnace and noting for every 50 mm the equilibrated temperature. As an example, Fig. 3-7 shows the for clinker burning relevant section of a temperature-distance profile of the furnace, with the heating zones (HZ1-5, Fig. 3-2) set to 1100, 1213, 1325, 1438 and 1550°C . Other furnace gas temperature profiles are shown in Appendix B. The distance specifies, to how far the SiC tube was moved into the furnace. The origin of the distance is set for the case that the Si tube is completely outside of the Al_2O_3 tube. Therefore, the distance includes a ~ 200 mm gap between the SiC and Al_2O_3 tube.

For all measured gas temperature profiles, temperatures of 850-900 °C are located before the first heating zone (HZ1 Fig. 3-2). This temperature area was used in further experiments as starting point, where samples were equilibrated for 30 min. The temperature rises steeply until a temperature of 1200 °C is reached approximately in the middle of the first heating zone (HZ1), after which the temperature increase is relatively linear. The maximum gas temperature in the heating furnace is always lower than the set temperature of the last heating zone (HZ5). In the case of Fig. 3-6 a maximum temperature of 1485 °C is reached. In order to obtain higher maximum gas temperatures the set temperatures of all heating zones needed to be increased, to keep the temperature difference from one heating zone to the next below 150 °C. A steeper temperature gradient could result in the breakage of the Al₂O₃ tube due to thermal shock.

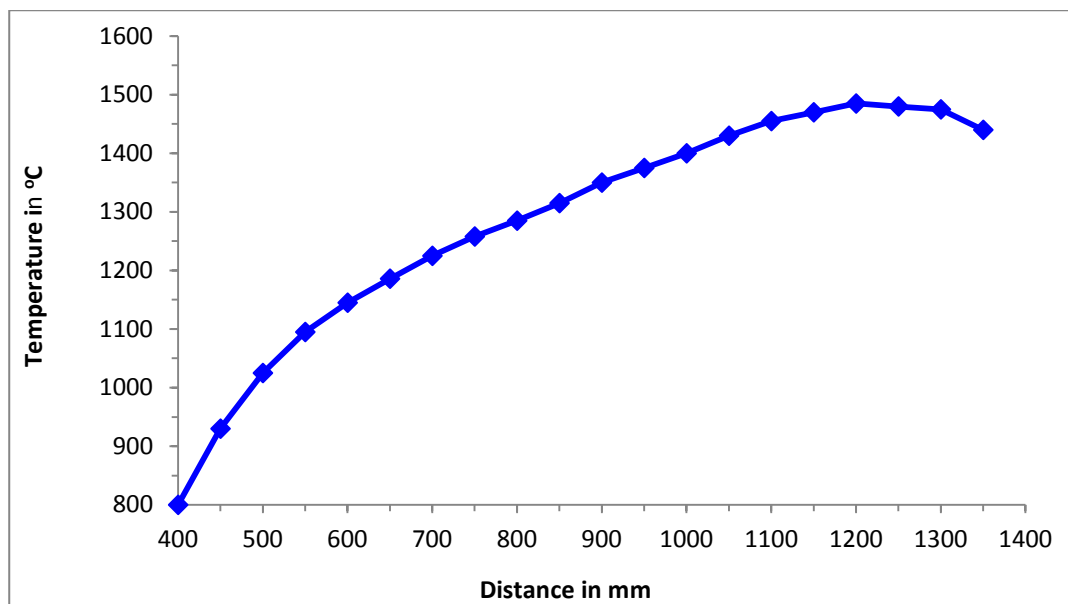


Fig 3-7: The temperature gradient in the heating furnace for HZ setting temperatures of 1100, 1213, 1325, 1438 and 1550 °C.

3.6.2 Gas Temperature inside the Pt/Rh-Crucible

In contrast to previous described furnace gas temperature measurement, the temperature change of the gas atmosphere in the Pt/Rh-crucible was measured, while the crucible, inserted into the SiC tube, was moved through the furnace with a certain velocity in non-rotational mode. The non-equilibrated temperature was noted every 50 mm following the steps of the furnace temperature

profile. In this way, a temperature profile similar to time dependent clinker burning experiments is obtained. First, the velocity of the SiC tube into the furnace was adjusted to create a linear outside temperature gradient for the SiC tube and Pt/Rh-crucible. Therefore, four different sections were set with different SiC tube velocities to adjust for the difference in steepness of the gas temperature increase in the heating furnace (Fig. 3-7). The linearized (calculated) temperature profiles for three different maximum heating times (35, 45, 60 min) are shown in Fig. 3-8. The indicated four sections between the five data points are related to Tab. 3-1 and Tab. 3-2. Here, section 2 reflects the linearization of the steep slope of the first three data point (400-500 mm) of the temperature profile of Fig. 3-7, which is related to a temperature increase from 800 to 1025 °C. As listed in Tab. 3-1, section 2 starts at a distance of 440 mm instead of at 400 mm similar to the temperature profile of Fig. 3-7. That is, because following measurements were started at 900 °C, which is in later clinker formation experiments (Chapter 4 and 5) the starting temperature. Sections 3, 4 and 5 represent the linearization of the slopes of data points from 500-750 mm, 750-1050 mm and 1050-1200 mm, which are related to temperature increases from 1025-1258 °C, 1258-1430 °C and 1430-1485 °C (Fig. 3-6, Tab. 3-5). The different velocities of the SiC tube for these four sections in order to achieve the linearized temperature-time profiles are listed in Tab. 3-6 for all three different maximum heating times. An additional section (section 1) was used for the positioning of the Pt/Rh-crucible at ~900 °C for equilibration.

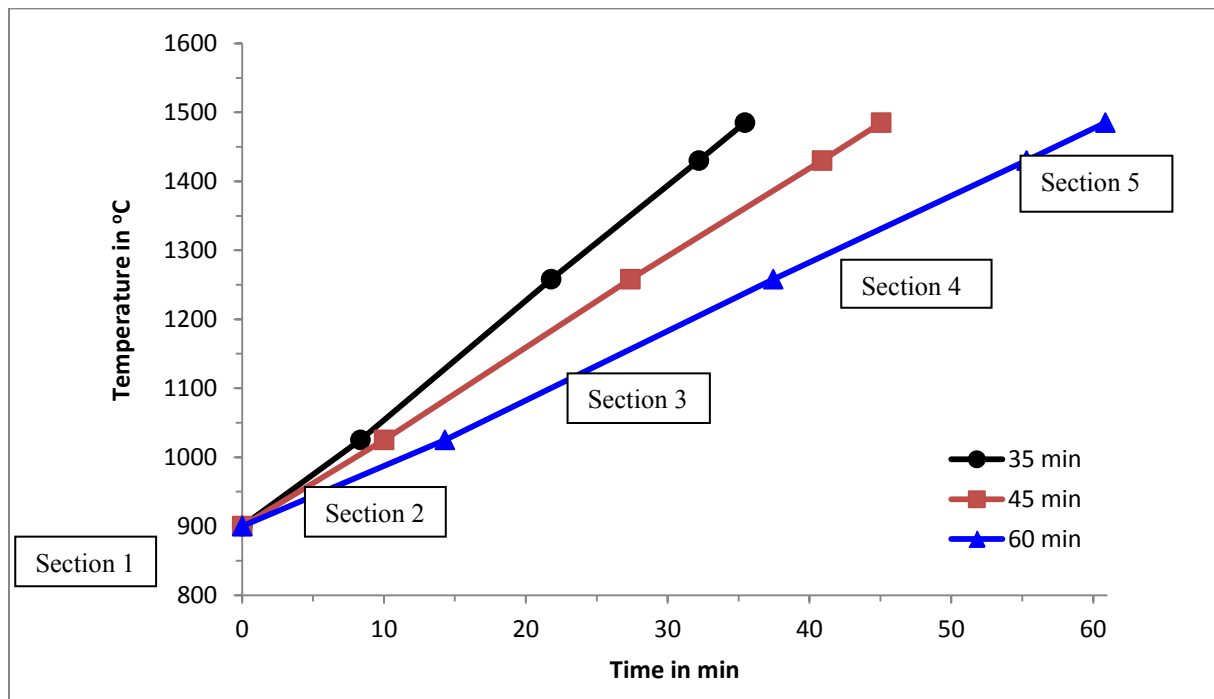


Fig. 3-8: Linearized temperature profiles for three different maximum heating times.

Tab. 3-5 List of five sections for with the related distances, temperature increase and heating rate for furnace temperature gradient linearization.

Total distance mm			800		
ΔT in °C			655		
Section	Distance in mm	Temperature in °C	Distance per section in mm	ΔT in °C	Heating rate in °C/mm
Section 1	0-440	25-900	440	875	1.99
Section 2	440-500	900-1025	60	125	2.25
Section 3	500-750	1025-1258	250	233	0.91
Section 4	750-1050	1258-1430	300	172	0.58
Section 5	1050-1200	1430-1485	150	55	0.36

Tab. 3-6 The related velocities for each section in order to achieve linearization of the furnace temperature gradient linearization.

Max. heating time	0.58 h	0.75 h	1 h
Section	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000	54000
Section 2	432	360	252
Section 3	1116	864	648
Section 4	1728	1332	1008
Section 5	2772	2160	1620
Average velocity in mm/s	1296	1008	756
Average heating rate in °C/s	1008	792	576

The thermocouple tip was placed inside the empty Pt/Rh-crucible, ensuring that the Pt-Pt/Rh-wires were not in contact with the crucible to avoid incorrect temperature read-out by the temperature controller. The temperature measurements were started after the gas atmosphere in the Pt/Rh-crucible was equilibrated to ~ 900 °C after 30 min at distance of 440 mm. Thereafter the SiC tube was moved through the different sections of the heating furnace with the related velocities (Tab. 3-2) and the temperature change was noted every 50 mm. The obtained temperature profiles for the three different heating times are shown in Fig. 3-9. As obvious, all three temperature profiles of the gas atmosphere (blue, red, green curves) in the Pt/Rh-crucible are similar and follow the temperature profile of the gas atmosphere of the heating furnace (purple curve). The small deviation of the temperature (~ 25 -55 °C) of the crucible gas atmosphere and the heating furnace gas atmosphere can be attributed to small differences between the placement of the thermocouple tip in the Pt/Rh crucible and in the SiC tube.

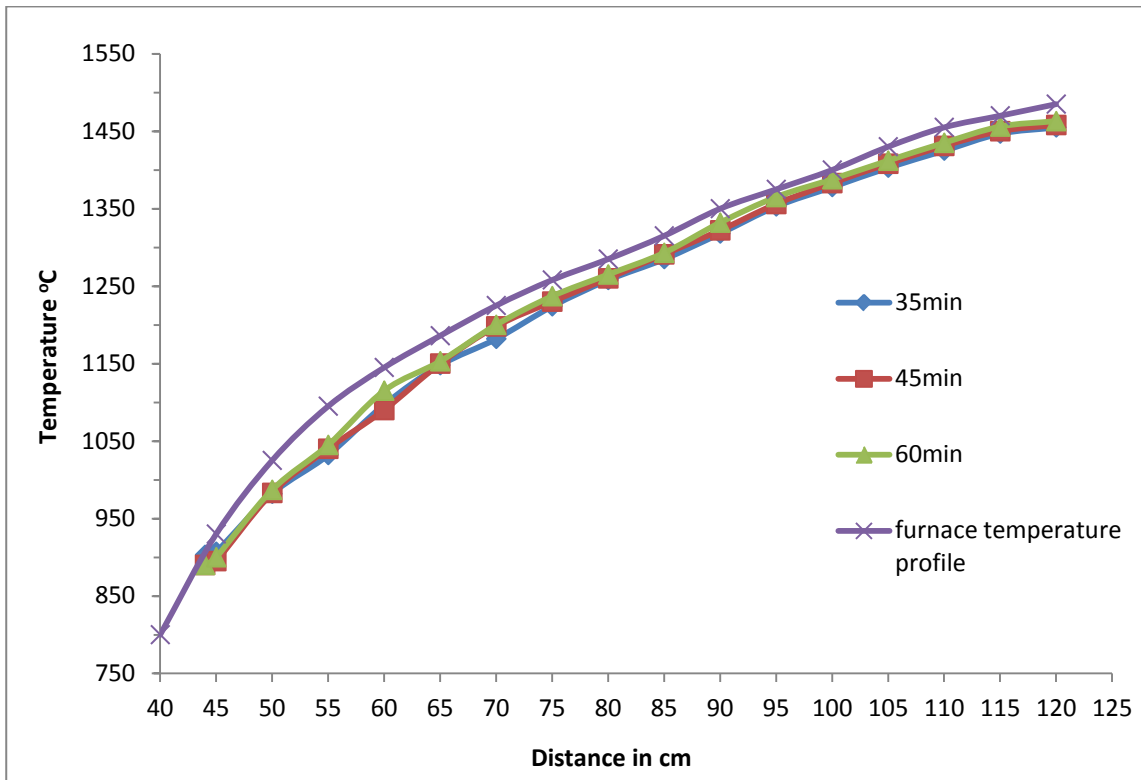


Fig. 3-9: The gas temperature gradients of 35, 45 and 60 min measurements in the Pt/Rh-crucible compared to gas atmosphere temperature in the heating furnace.

3.6.3 Solid Material Temperature

Here, the temperature increase of the solid material inside the Pt/Rh-crucible, raw meal/clinker, and of the Pt/Rh-crucible walls were measured. The measurements were somewhat similar to the previously described gas atmosphere temperature measurements in the Pt/Rh-crucible, except that temperature profiles were only recorded for a maximum heating time of 45 min. In the case of the raw meal/clinker temperature measurement, the tip of the thermocouple was inserted into the Pt/Rh-crucible and embedded into cement raw meal. For the crucible wall temperature measurement, the thermocouple tip was brought into contact with the inside walls of the Pt/Rh-crucible. Both measurements were carried out using the linearized temperature profile of the third column of Tab. 3-2 (45 min). As before, the SiC tube with the Pt/Rh-crucible was positioned to a distance of 440 mm and left to equilibrate to ~ 900 °C within 30 min. Thereafter, the SiC tube with the crucible was moved through the heating furnace noting the temperature change every 50 mm. The obtained temperature profiles are shown in Fig. 3-10 and 3-11. Similar as before, both temperature profiles

follow the run of the curve of the heating furnace temperature profile with some small deviations, attributed to slight differences of the thermocouple placement. Most importantly, the temperature profile of the solid material (cement raw meal/clinker) shows, that the material heats up quickly to the furnace gas temperature as it is moved through the heating furnace. Therefore for further experiments, it is only necessary to measure the gas temperatures profiles of the heating furnace, assuming that the temperature increase of the solids inside the Pt/Rh-crucible is similar.

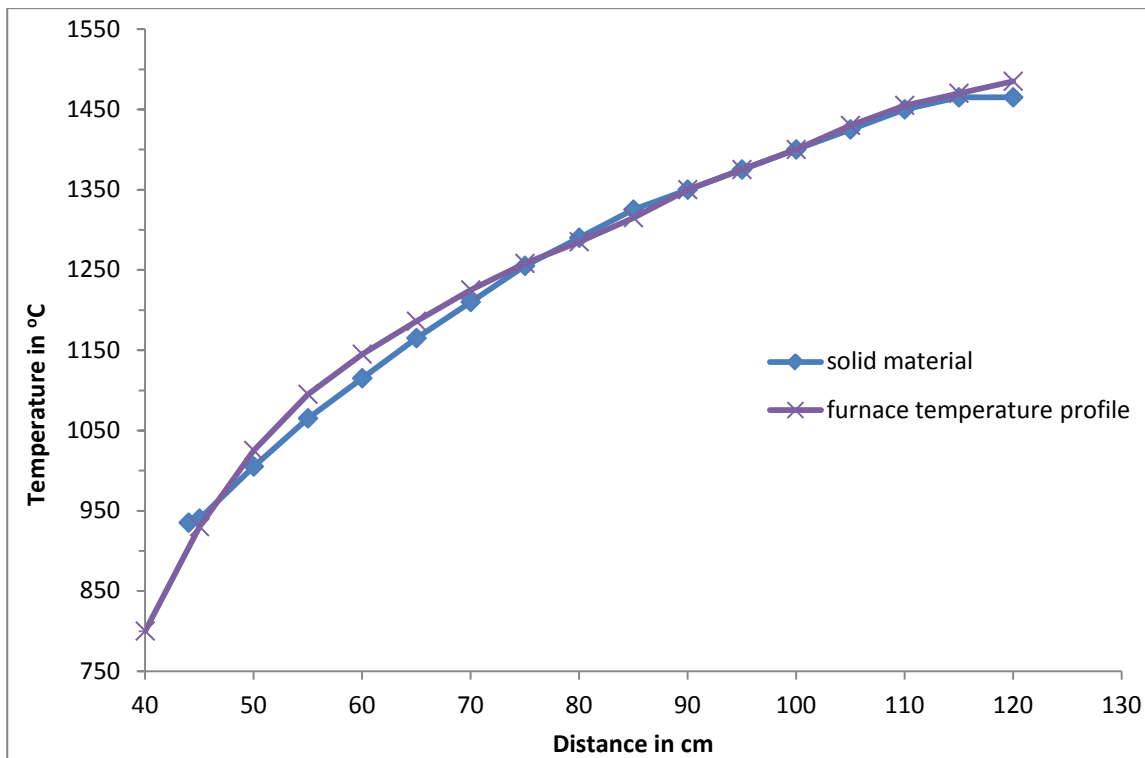


Fig. 3-10: The temperature gradient of the solid material in the Pt/Rh-crucible compared to gas atmosphere temperature in the heating furnace.

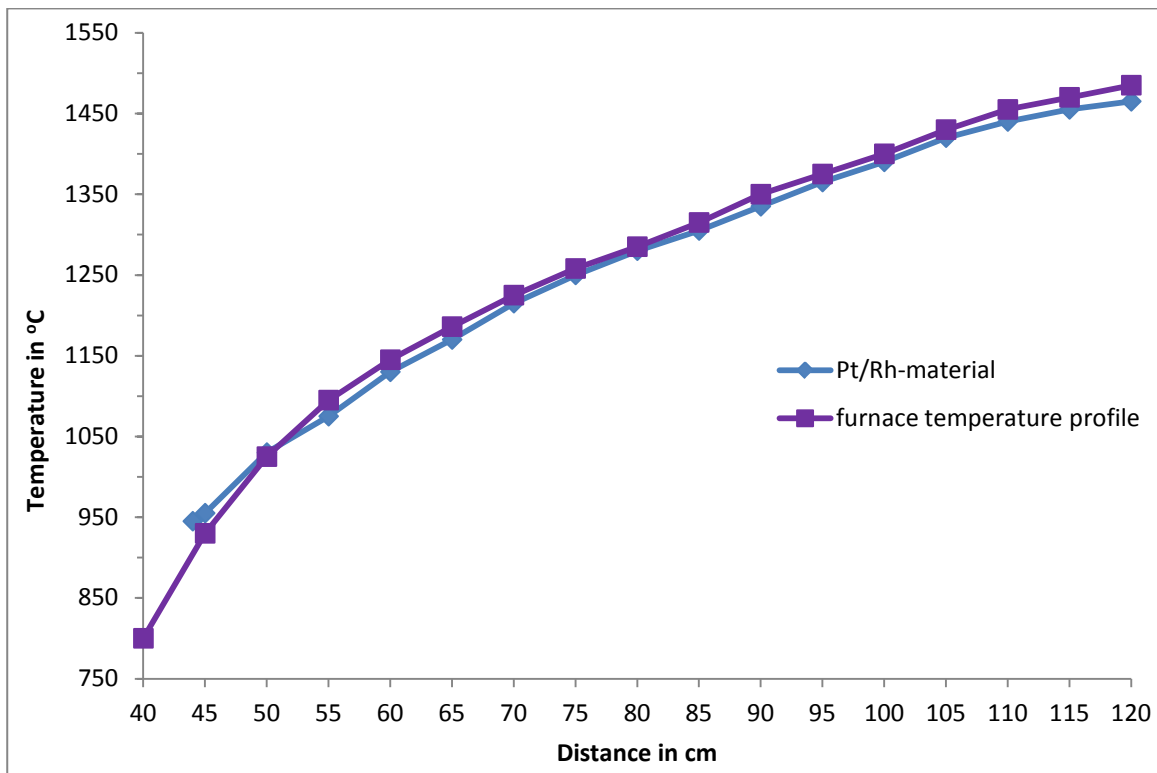


Fig. 3-11: The temperature gradient of the Pt/Rh-crucible wall compared to gas atmosphere temperature in the heating furnace.

3.7 References

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Chapter 4

Reproducibility and Repeatability Tests in the RKS

4.1 Reproducibility of Clinker Formation in the RKS

Clinker formation is a very complex process, consisting of several sub-steps and depending on several different factors. Thus, it was of utmost importance to verify the consistency of clinker produced in the rotary kiln simulator (RKS) in comparison to clinker formed in other heating furnaces. The reproducibility of clinker burning in the new RKS was evaluated against clinker formation in an ordinary lab-scale heating furnace. Here, clinker samples from burnability tests at FLSmidth laboratories were used for comparison. Since these burnability tests are carried out isothermally and stationary (without rotation) clinker burning under similar conditions were carried out with the RKS.

4.1.1 Experimental Procedure

The clinker formation was carried out using an industrial “ready to use” raw meal from a cement plant and is denoted as R. It was characterized at the laboratories of FLSmidth in Dania (Denmark). Detailed raw meal properties, i.e. the chemical composition, the resulting Lime Saturation Factor (LSF), Silica module (M_S), Alumina module (M_A) and the particle size fractions are listed in Tab. 4-1. A batch of powdery raw meal (ca. 150 g) was divided into 6 samples. To each sample, water was added and mixed to obtain a thick paste. Nodules of ~ 7 mm in diameter were hand-prepared from the thick pastes for each sample. The nodules were dried at 85 °C for 1 h. Thereafter, each sample was put into a Pt/Au-boat and calcined at 950 °C for 30 min in air in a chamber oven. Right after calcination of a sample, it was placed into either the Pt/Rh-crucible or into a Pt/Au-boat, which then was inserted into the SiC tube of the RKS. The heating zones of the furnace were all set to one temperature, i.e. 1400, 1450 or 1500 °C. The SiC tube was inserted into the center of the heating furnace within less than 1 min. The sample was burned for 30 min under oxidizing conditions (N_2 75% and O_2 25%). Thereafter, it was removed (within 25 sec) and cooled to room temperature with compressed air (within 2 min). The clinker samples were stored in a desiccator for further sample analysis. Two samples were burned for each temperature, one in the special designed Pt/Rh-crucible and one in an ordinary Pt/Au-boat to evaluate possible differences of the clinker composition due to the use of different crucibles. Pt/Au- boats are generally used in ordinary burnability tests.

The samples were analyzed by XRF for their chemical composition and for the clinker phase composition by XRD.

Tab. 4-1 Properties of the industrial raw meal from the cement plant R.

Chemical Composition in wt.%		Particle size fractions in wt.%	
CaO	41.7	>200 μ m	1.8
SiO ₂	14.1	>125 μ m	6.5
Al ₂ O ₃	3.47	>90 μ m	12.5
Fe ₂ O ₃	2.45	>45 μ m	27.1
MgO	1.98	Acid insoluble >45 μ m	9.8
Mn ₂ O ₃	0.01	Composition of acid insoluble residue in wt. %	
TiO ₂	0.21		
P ₂ O ₅	0.02		
K ₂ O	0.13		
Na ₂ O	0.13	Quartz >45 μ m	3.0
SrO	0.03	Flux minerals >45 μ m	1.7
Cl ⁻	0.12	Other silicates >45 μ m	5.1
S	0.04	Concentration of CaCO ₃	4.0
LOI	35.8	grains >125 μ m	
Clinker Moduli		Unreacted CaO concentration in wt.%*	
LSF	92	1400 °C	3.3
SR	2.4	1450 °C	1.8
AR	1.4	1500 °C	1.1

*concentration derived by Free lime analysis.

4.1.2 Results

The clinker phase compositions of the samples burned in the new RKS are listed in Tab. 4-2. The clinker phase compositions of samples burned in the specially designed Pt/Rh-crucible and in an ordinary Pt/Au boat are similar and the results listed in Tab. 4-2 are the average clinker phase concentrations of the two samples heat treated at the same temperature. The clinker phase composition of samples from burnability tests at the laboratories of FLSmidth are listed in Tab. 4-3. Both test series show similar tendencies although the actual concentrations of clinker phases for samples burned at the same temperature differ, especially in C₃A and unreacted CaO. The important, i.e. temperature dependent phases are alite (C₃S), belite (C₂S) and unreacted CaO. In general, the concentration of alite increases with increasing temperature, whereas the belite

concentration and the unreacted CaO concentration decrease. These results reflect the common knowledge of the temperature influence on clinker phase formation: the higher the temperature the more complete the reaction of CaO with C_2S to form C_3S ^{1,2}. The comparison of the RKS burned samples with the burnability samples reveals slight differences in the C_3S - and C_2S phase concentrations of samples burned at the same temperature, especially of those prepared at 1400°C. This is in the temperature range where significant clinker melt formation occurs and the C_3S formation mechanism changes from (mainly) solid-state reactions to solid-liquid/liquid-state reactions. In this temperature range, small differences in the sample preparation, especially raw meal mixing and hand nodulization, resulting in different degrees of homogeneity, will have a more pronounced effect on the final clinker phase composition at the lower temperature than at higher temperatures (1450 and 1500 °C). Inhomogeneities in the unburned samples are more likely to be outbalanced by higher melt concentrations at higher temperatures due to extensive inner motion and mixing of material.

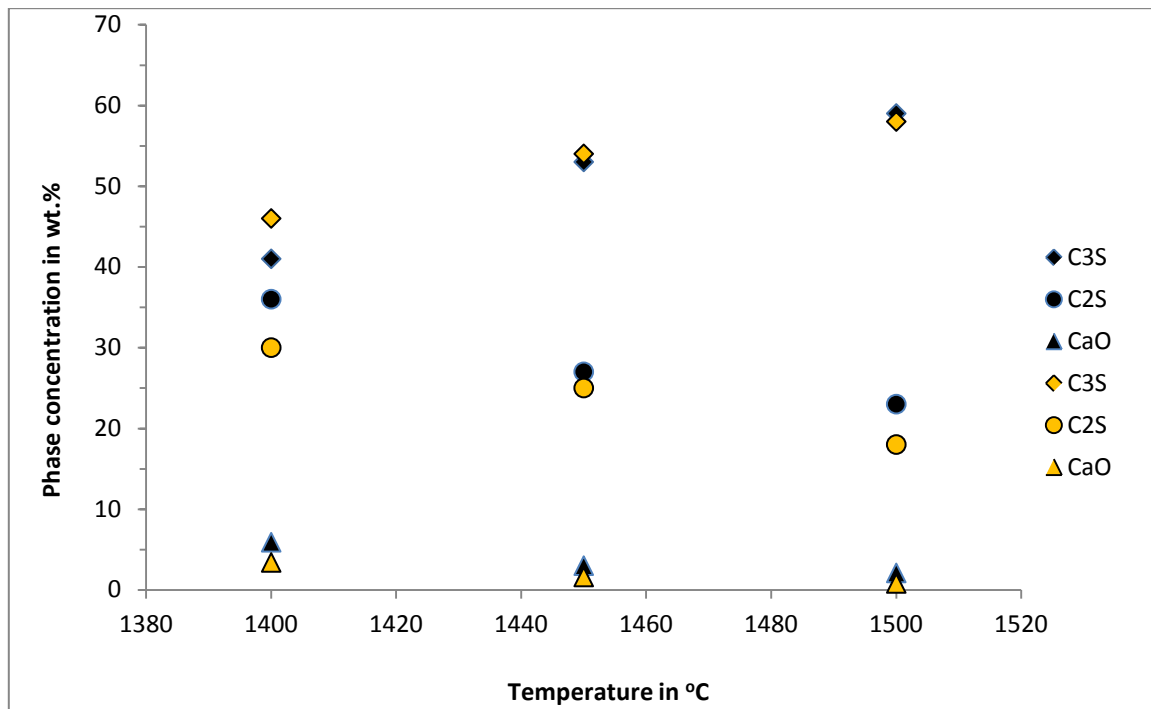
A bigger difference in concentration was observed for the C_3A and CaO phases. The burnability test (in Table 4-3) was conducted only once for each temperature and an uncertainty for the results was hence not obtained. The concentration of the C_3A phase (R-B 1400 - R-B 1500) fluctuates significantly without a noticeable tendency with respect to the temperature. Furthermore, the concentration should be expected to be rather constant for this phase: alumina and iron oxide mainly form C_3A (and C_4AF ; the intermediate $C_{12}A_7$ was not observed) at temperatures <1400 °C. Higher temperatures thus only result in melting (and recrystallization upon cooling) but should not influence the amount. Thus, the fluctuation in the C_3A concentration indicate, that the burnability test (R-B 1400 - R-B 1500) features higher uncertainties than the samples I-1400 - I-1500 show, i.e. latter are considered to be more reliable. In contrast, the CaO concentrations of the samples R-B 1400 - R-B 1500 are similar to the concentration derived by Free lime analysis (Tab. 4-1), indicating a higher accuracy of the CaO concentrations in Tab. 4-3. However, differences between the two test series are mostly within reasonable deviations ($\pm 2-3$ wt.-%) and therefore the clinker phase compositions of the samples prepared in the different setups are nearly similar and thus the setup exhibits satisfactory reproducibility. A comparison of the reproducibility of the clinker phases is shown in Fig. 4-1.

Tab. 4-2 Clinker phase composition of samples (denoted in Roman numerals) burned for reproducibility tests in the RKS.

Sample name	Burning temperature	Clinker phase concentration in wt.-%						
		C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
I-1400	1400	41 ± 3	36 ± 5	12 ± 2	2.6 ± 1.7	5.9 ± 0.6	1.7 ± 0.3	0.1 ± 0.4
II-1450	1450	53 ± 3	27 ± 1	12 ± 0	2.3 ± 2.0	3.0 ± 0.4	1.7 ± 0.0	0.9 ± 0.3
III-1500	1500	59 ± 5	23 ± 5	13 ± 1	2.6 ± 2.4	2.1 ± 0.7	1.7 ± 0.4	-0.9 ± 1.4

Tab. 4-3 Clinker phase composition of samples of burnability test (“B”) at FLSmidth laboratories.

Sample name	Burning temperature	Clinker phase concentration in wt.-%						
		C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
R-B 1400	1400	46	30	12	6.2	3.4	1.5	-0.1
R-B 1450	1450	54	25	15	3.6	1.6	1.2	0.2
R-B 1500	1500	58	18	11	8.0	0.8	1.0	3.9

**Fig. 4-1:** Reproducibility of the C₃S, C₂S clinker phases as well as unreacted CaO. Dark icons represent the samples of Tab. 4-2 and the bright icons represent the samples of Tab. 4-3.

4.2 Repeatability Tests of Clinker Burning in the RKS

The repeatability of clinker burning with the RKS was tested in a series of different experiments. In the first experiments the operation stability of the setup over time was tested. This test was carried out without rotation and with a raw meal made by mixing of purchased chemicals. This allows not only control of the burning temperature and burning time but also of the raw meal composition and homogeneity, all of which are vital parameters influencing the final clinker composition. The next test included the rotation velocity and was carried out with industrial raw meal under isothermal conditions. At last, industrial raw meal was burned under non-isothermal conditions at a temperature profile from ~900-1540 °C, in rotational mode. An overview of the varied parameters is shown in Tab.4-4.

Tab. 4-4 An overview of the changed parameters for each repeatability test.

	Parameters changed					
	Composition		Rotation		Temperature	
Subsection	Industrial raw meal	Chemical mixture	With	Without	Isothermal	Gradient
5.2.1 a)		X		X		X
5.2.1 b)	X		X		X	
5.2.1 c)	X		X			X

4.2.1 Experimental Procedure

a) Clinker Burning from Chemical Mixture in Non-rotational Mode³

Six samples were prepared in total: three samples were burned consecutively within a one hour interval and three samples were burned with the heating furnace of the setup being shut down and started up in between. The used raw meal contained CaCO_3 , SiO_2 , Al_2O_3 and Fe_2O_3 as major compounds as well as MgO , Na_2CO_3 , K_2CO_3 , $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, Na_3PO_4 as minor compounds and was prepared from purchased chemicals (Tab. C-1 in Appendix C). The composition of the raw meal batch is listed in Tab. 4-5. The LSF, M_S and M_A as well as the potential clinker phase composition, calculated with the Bogue equations, are listed in Tab. 4-6. An aqueous slurry of the compound mixture was stirred for 24 h to obtain a high homogeneity. The batch was dried for 24 h at 85 °C, and divided into 6 samples. To each powder sample a small amount of water was added to form a

paste like mixture from which small spherical granules (~7 mm in diameter) were hand-prepared. After drying, each sample was pre-calcined at 950 °C for 30 min. The calcination degree was ~80 %. The pre-calcined sample was placed in an ordinary Pt/Au-boat and inserted into the furnace facing end of the SiC tube of the motion system. The heating zones of the setup furnace were set as followed:

	Heating Zone				
	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C	1100	1213	1325	1438	1550

This resulted in a furnace gas temperature profile from ~900-1450 °C (temperature profile 1 in Appendix B). The sample was moved into the furnace to the spot of ~900 °C, where it equilibrated and completed calcination within 30 min. Clinker burning was conducted in oxidizing atmosphere (75 % N₂, 25 % O₂). All samples were burned in non-rotational mode at different rates (Tab. B-2 in Appendix B (program 2; 30 min)). After clinker burning the Pt/Au-boat was instantly removed from the SiC tube and cooled down to room temperature with compressed air flushing along the outer Pt/Au-boat walls. The samples were transferred into a plastic flask and stored in a desiccator for further analysis. The samples were analyzed for the chemical composition (XRF and free lime analysis) and for the clinker phase composition (XRD).

Tab. 4-5 Raw meal composition.

Chemicals	wt. %	oxides	wt. %
CaCO ₃	77.31	CaO	66.99
SiO ₂	14.65	SiO ₂	22.68
Al ₂ O ₃	3.26	Al ₂ O ₃	5.04
Fe ₂ O ₃	1.63	Fe ₂ O ₃	2.52
MgO	0.98	MgO	1.52
Na ₂ CO ₃	0.46	Na ₂ O	0.31
K ₂ CO ₃	0.67	K ₂ O	0.59
CaSO ₄ *2H ₂ O	0.98	SO ₃	0.28
Na ₃ PO ₄	0.05	P ₂ O ₅	0.07

Tab. 4-6 LSF, M_S and M_A and the potential clinker phase composition (obtained from the Bogue equations) of the raw meal.

			Potential clinker phase composition in wt. %			
LSF	SR	AR	C ₃ S	C ₂ S	C ₃ A	C ₄ AF
94	3	2	63	18	9	8

b) Isothermal Clinker Burning from Industrial Raw Meal in Rotational Mode

The same industrial raw meal as before (section 4.1) was used for this test. The chemical composition as well as LSF, M_S and M_A are listed in Tab. 4-1. A batch of powdery raw meal (ca. 650 g) was calcined at 950°C for 45 min in a chamber oven with frequent mixing in between. The calcined material was quickly cooled to room temperature, sieved through a 250 µm mesh to break up lumps and stored in a closed container to minimize CO₂ uptake from air. Ca. 20 g of the calcined material were inserted into the Pt/Rh-crucible, which was then placed into the SiC tube of the RKS. The heating zones were all set to one temperature, i.e. 1400, 1450, 1500 or 1550 °C. The SiC tube was rotated with 5 rpm and inserted into the center of the heating furnace within less than 1 min. The sample was burned for 30 min under oxidizing conditions (75% N₂ and 25% O₂). Thereafter, it was removed (within 25 sec) and cooled to room temperature with compressed air (within 2 min). The clinker samples were stored in a desiccator for further sample analysis. Three samples were burned for each temperature. The samples were analyzed for the chemical composition (XRF and free lime analysis) and for the clinker phase composition (XRD).

c) Clinker Burning from Industrial Raw Meal in Rotational Mode with a Temperature Gradient

A batch of raw meal R (chemical composition and LSF, M_S and M_A in Tab. 4-1) (ca. 100 g) was calcined at 950°C for 30 min in a chamber oven. The calcined material was quickly cooled to room temperature, sieved through a 250 µm mesh to break up lumps and stored in a closed container to minimize CO₂ uptake from air. Ca. 20 g of the calcined material were inserted into the Pt/Rh-crucible, which then was placed into the SiC tube of the RKS. The heating zones of the setup furnace were all set as followed:

	Heating Zone				
	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C	1200	1300	1400	1500	1600

This resulted in a furnace gas atmosphere temperature profile of ~ 900 - 1540°C (temperature profile 1 in Appendix B). The SiC tube with the sample was moved to $\sim 900^{\circ}\text{C}$ to equilibrate the sample for 30 min. Thereafter, the sample was moved through the heating furnace with a linearized temperature profile (see section 3.5). The velocities are listed in Tab. B-4 in Appendix B (program 3; 30 min). The SiC tube was rotated with 5 rpm simultaneously to the motion along the horizontal axis. The sample was burned for 30 min under oxidizing conditions (75% N_2 and 25% O_2). Thereafter, it was removed (within 25 sec) and cooled to room temperature with compressed air (within 2 min). The clinker samples were stored in a desiccator until sample analysis. In total, three samples were burned under the same conditions in a one day interval. The samples were analyzed for the chemical composition (XRF and free lime analysis) and for the clinker phase composition (XRD).

4.2.2 Results

The samples of the repeatability test are denoted with Arabian numbers. The following codes were used to for the various experimental conditions (Tab. 4-7).

Tab. 4-7 Sample denotation.

Parameter	Code	Explanation	Code	Explanation
Raw meal	C	Mixture of purchased Chemicals	In	Industrial raw meal
Temperature (subscript)	Is	Isothermal furnace temperature	G	Temperature Gradient in heating furnace
SiC-tube rotation	S	Static, non-rotational mode	R	Rotational mode

a) Clinker Burning from Chemical Mixture in Non-rotational Mode³

The clinker phase compositions of the six samples (C_GS 1-6) are listed in Tab. 4-8 and shown in Fig. 4-2. The first three samples (C_GS 1-3) are burned consecutively with 1 h between each clinker burning experiment, the last three (C_GS 4-6) are burned with a shut-down and startup of the setup in between. The clinker phase compositions of all samples show only minor differences in the concentration of all clinker phases as the uncertainty of the average concentration (Average C_GS)

outlines. These fluctuations can be attributed to the general uncertainty of the XRD method. The unreacted CaO concentration determined by the Free lime analysis (Tab. 4-9) show a significant smaller uncertainty, demonstrating the conclusion that the setup operation is stable over the time in which the experimental series is carried out (ca. 5 days).

Tab. 4-8 Clinker phase composition determined by XRD.

Sample name	Clinker phase concentration in wt.-%						repeated burning after
	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	Residual	
C _G S 1	68	15	4.7	13	2.1	-2.7	0
C _G S 2	65	15	5.3	11	2.0	1.8	1 hour
C _G S 3	68	14	4.7	12	1.8	-0.7	2 hour
C _G S 4	69	15	4.3	13	2.2	-2.7	1 day + shut down
C _G S 5	70	14	4.2	13	2.0	-3.9	2 days + shut down
C _G S 6	68	15	4.9	12	1.5	-0.8	3 days + shut down
Average C _G S	68 ± 3	15 ± 1	4.7 ± 0.8	12 ± 2	1.9 ± 0.5	-1.5 ± 4.1	

Tab. 4-9 Unreacted CaO in samples determined by Free lime analysis.

Sample name	CaO in wt.-%
C _G S 1	2.0
C _G S 2	2.0
C _G S 3	2.0
C _G S 4	2.1
C _G S 5	2.2
C _G S 6	2.8*
Average C _G S	2.1 ± 0.2

* outlier as identified by student's t-test; thus not included in average concentration.

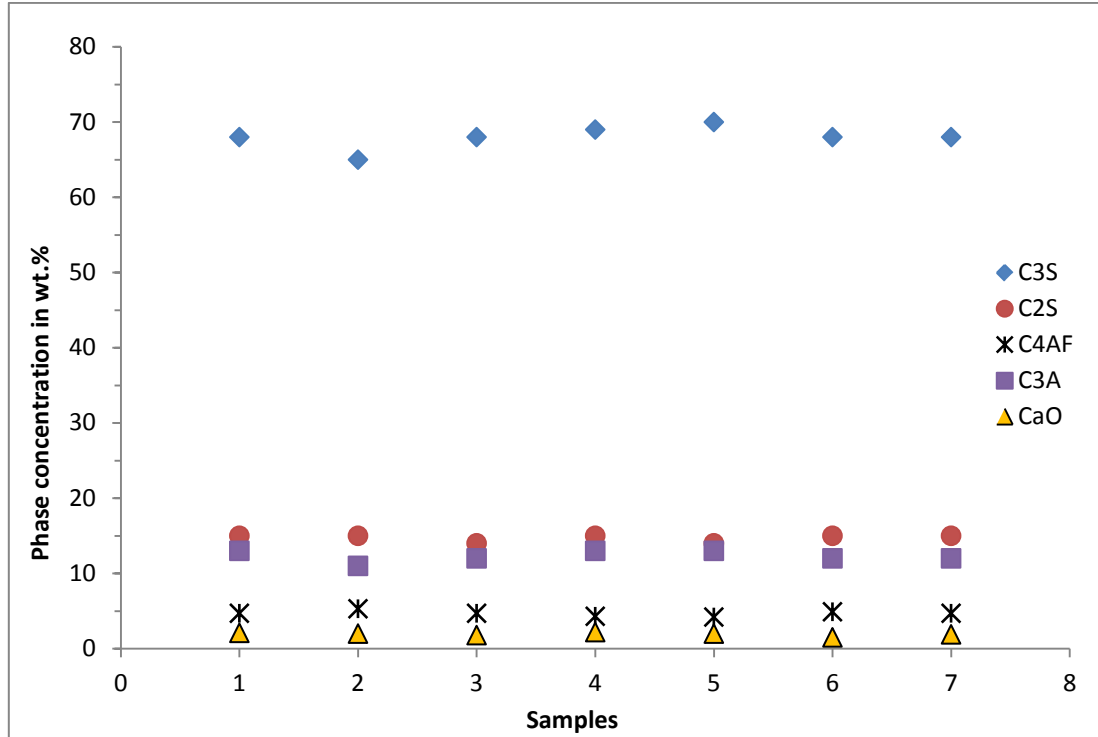


Fig. 4-2: The clinker phase composition of the samples C_GS 1 - C_GS 6 as well as of the average C_GS.

b) Isothermal clinker burning from industrial raw meal in rotational mode

The clinker phase compositions of all samples burned isothermally but using the rotational mode are listed in Tab. C-2 and Tab. C-3 (Appendix C). Tab. 4-10. Tab. 4-11 lists the average clinker phase concentrations of samples prepared at the same temperature, which are also shown in Fig. 4-3. Despite some smaller uncertainties, satisfactory repeatability was found, i.e. the rotational mode at isothermal clinker burning causes only slight differences in the clinker composition. Note that samples heat treated at 1550 °C should contain more C₃S and less unreacted CaO (Tab. 4-10) than samples burned at 1500 °C. The difference found here is statistically not significant from XRD analysis. But the Free lime analysis suggests also here that the expected tendency exists (Tab. 4-11).

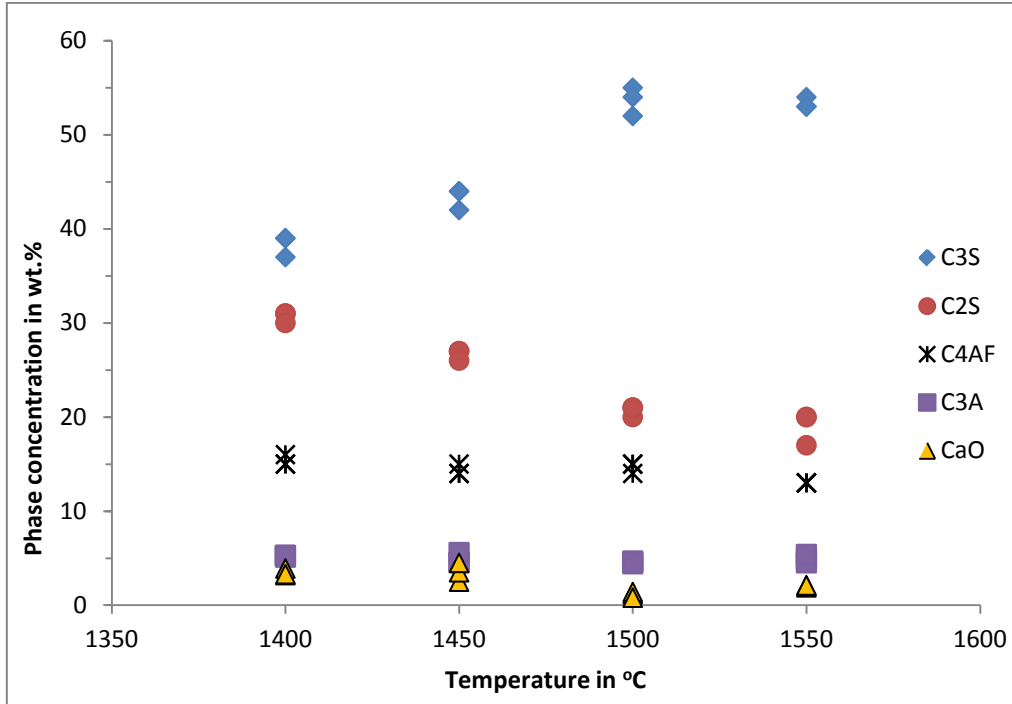


Fig. 4-3: The clinker phase composition of clinker samples isothermally produced at rotational mode. Clinkerization was repeated 3 times at each temperature.

Tab. 4-10 Average XRD clinker phase composition and uncertainty of sample prepared at the same temperature.

Sample name	Burning temperature	Average clinker phase concentration in wt.%						
		C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
In _{IS} R 1-3	1400	38 ± 2	31 ± 1	15 ± 1	5.2 ± 0.2	3.5 ± 0.8	1.4 ± 0.3	5.6 ± 1.4
In _{IS} R 4-6	1450	43 ± 3	27 ± 1	14 ± 1	4.9 ± 1.2	3.5 ± 2.0	1.5 ± 0.3	6.0 ± 2.2
In _{IS} R 7-9	1500	54 ± 2	21 ± 1	15 ± 1	4.6 ± 0.3	1.0 ± 0.4	1.6 ± 0.6	3.4 ± 3.5
In _{IS} R 10-12	1550	54 ± 3	19 ± 3	13 ± 1	4.9 ± 0.9	2.0 ± 0.2	1.3 ± 0.5	5.8 ± 5.2

Tab. 4-11 Average unreacted CaO concentration and uncertainty of sample prepared at the same temperature.

Sample name	CaO in wt.%
In _{IS} R 1-3	5.8 ± 0.6
In _{IS} R 4-6	4.6 ± 1.7
In _{IS} R 7-9	2.6 ± 0.0
In _{IS} R 10-12	1.7 ± 0.2

c) Clinker Burning from Industrial Raw Meal in Rotational Mode at a Temperature Gradient

The clinker phase concentrations of samples prepared from industrial raw meal burned with a temperature gradient in rotational mode are listed in Tab. 4-12 and the unreacted CaO concentration (determined by Free lime analysis) is listed in Tab. 4-13. The concentrations of nearly all clinker phases show significant fluctuations as the uncertainty of the average concentration outlines. Note that the Free lime analysis usually gives more reliable analysis data, indicating that the observed fluctuations also originate from the sample itself and not only from the XRD analysis. These uncertainties are higher than in the previous test indicating, that the rotational mode together with non-isothermal heating introduces more complex experimental conditions for the clinker formation and its repeatability than both conditions separately. Because the bed material experiences a temperature gradient (although rather small) in the Pt/Rh-crucible and due to the rotational mode it is mixed forth and back in the reactor. These processes may be difficult to control from one sample to another, thus increasing the uncertainty compared to previous experiments. However, the experimental uncertainties are still satisfactory overall.

Tab. 4-12 Clinker phase composition determined by XRD. The last row lists the average and the uncertainty of the clinker phase concentrations.

Sample name	Clinker phase concentration in wt.-%						
	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
In _G R 1	43	27	15	5.1	7.9	1.4	0.8
In _G R 2	41	27	13	5.6	8.0	1.4	3.6
In _G R 3	39	32	13	5.3	7.2	1.6	1.4
Average In _G R	42 ± 4	29 ± 6	14 ± 2	5.3 ± 0.5	7.7 ± 0.9	1.5 ± 0.2	1.9 ± 2.9

Tab. 4-13 Unreacted CaO in samples determined by Free lime analysis. The last row lists the average and the uncertainty of the clinker phase concentrations.

Sample name	CaO in wt.-%
In _G R 1	6.4
In _G R 2	5.8
In _G R 3	5.1
Average In _G R	5.8 ± 1.3

4.3 Summary

Isothermal clinker burning in the RKS without rotation results in only minor differences in mineralogical composition compared to clinker burning in an ordinary lab-scale heating furnace, thus the setup exhibits reasonable reproducibility.

The repeatability of non-isothermal clinker burning without rotation is satisfactory. The setup operates stable over time. Similar conclusion can be drawn for isothermal clinker burning with rotational mode.

Experimental condition including both non-isothermal heat treatment and rotational mode result in higher uncertainties, i.e. higher differences in mineralogical composition, than for clinker burning featuring only one of these parameters. Despite the higher uncertainties, the repeatability of clinker burning under non-isothermal, rotational experimental conditions is still acceptable.

Overall, the reproducibility (in comparison to other lab-scale furnaces, but not an ICRK) and repeatability of clinker burning in the RKS is satisfactory.

4.4 References

- (1) Bye G.C. *Portland cement Composition, production and preparation*. 1st ed. Pergamon Press Ltd:Oxford, **1983**.
- (2) Taylor H.F.W. *Cement Chemistry*. 2nd ed. Academic Press Thomas Telford: London, **1997**, ISBN: 0-7277-2592-0, p. **70**.
- (3) Jørgensen L. Clinker porosity. Master thesis carried out at the Institute of Chemical and Biochemical Engineering. 2010

Chapter 5

Simulation of Industrial Clinker Burning

Up to now Portland cements (CEM I and CEM II) are the most produced cements yearly ¹. The main constituent of these cements is clinker, which is composed of 40-80 wt.% C_3S , 10-50 wt.% C_2S , 0-15 wt.% C_3A and 0-20 wt.% C_4AF ¹. Additionally, clinker may contain, among other minor compounds, 0-3 wt.% unreacted CaO ¹. The following investigations are aiming at simulating industrial clinker formation in the RKS, i.e. the clinker phase composition of the RKS experiments should be reasonably close to the composition of industrial clinker as described above. Specifically, the aim is to achieve high C_3S concentration in clinker, which is the most important strength giving clinker phase of Portland cement. Therefore, the C_3S concentration, determined by XRD analysis, and the unreacted CaO concentration, determined by XRD and Free lime analysis, is followed as a measure of the progress/completeness of alite phase formation. CaO is consumed by the formation of C_3S (see Chapter 2), thus the general aim is to reach an unreacted CaO concentration below 1.5 wt.% in clinker samples.

5.1 Comparison of General Clinker Properties Developed in the RKS and ICRK

The following sections (5.2 - 5.5) deal with clinker formation under different experimental conditions in the RKS. Dependent on the chosen experimental conditions, clinker samples show characteristic chemical and mineralogical compositions. However, some clinker properties were for all samples similar and will be therefore summarized shortly. Further discussions on those properties in later sections follow only, if the extent of a property was found to be dependent on the experimental conditions.

The rotation motion of the setup resulted always in the formation of spherical agglomerates of different size (Fig. 5-1) and in the formation of lining on the inside of the reactor wall (i.e. the Pt/Rh-crucible; Fig. 5-2). The clinker agglomerates are formed and grow in size by rolling of particles or small agglomerates on top of the bed material, collecting matter (particles or small agglomerates) sintering together with rolling agglomerate (see subsection 5.3 and 5.4). The formation of agglomerates during clinkerization is an essential difference to common clinker formation investigations using hand-nodule agglomerates. It enables also the study of physical clinker properties besides the chemical and mineralogical properties.



Fig 5-1: Clinker agglomerates, which were formed rolling on top of the lining in the crucible (left) and a clinker agglomerate with a diameter > 4 mm (right). Its formation occurred by sintering of smaller agglomerates (black arrow) together with a bigger core agglomerate. Black pores are clearly visible (white arrow).

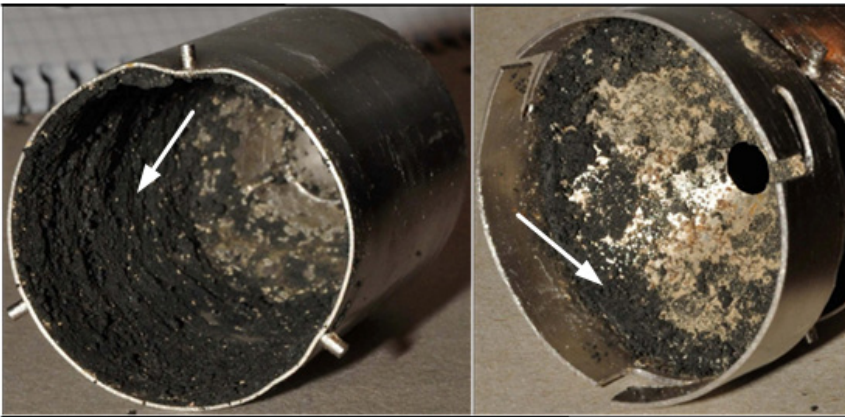


Fig. 5-2: The inside of the platinum crucible after test burning. On the walls occurred lining of the solid and partly molten material.



Fig. 5-3: Left: dense agglomerates of industrial clinker. Right: The magnification of one agglomerate with a diameter ~ 17.5 mm.

All clinker samples consisted of the typical crystal phases, i.e. C_3S , C_2S , C_3A , C_4AF and additionally unreacted CaO . Furthermore the MgO (periclase) crystal phase was also found in most samples. The distribution of the clinker crystal phases within the agglomerates is shown in Fig. 5-4 (magnification of 50x / 200x and special hydrofluoric acid (HF) treated). The agglomerates consist of high amounts of C_3S (brownish phase). Within the C_3S matrix, C_2S crystals or clusters are distributed (bluish phase). The C_3S and C_2S crystals are surrounded by C_3A and C_4AF (white areas), which formed the clinker melt phase during the heat treatment. Fig. 5-4 and Fig. 5-1 also show the main difference between clinker formed in the RKS and industrial clinker. Clinker produced in the RKS featured a high macro-porosity in the range of $\sim 800 \mu m$ (black spots in Fig. 5-4, pores in Fig. 5-1). In contrast, industrial clinker is a very compact product (Fig. 5-3). This is mainly a consequence of the scale: in the industrial rotary kiln the high weight compresses the material intensifying sintering processes. This is an important difference to the RKS, where 25 g of material develop only negligible pressure on the material.

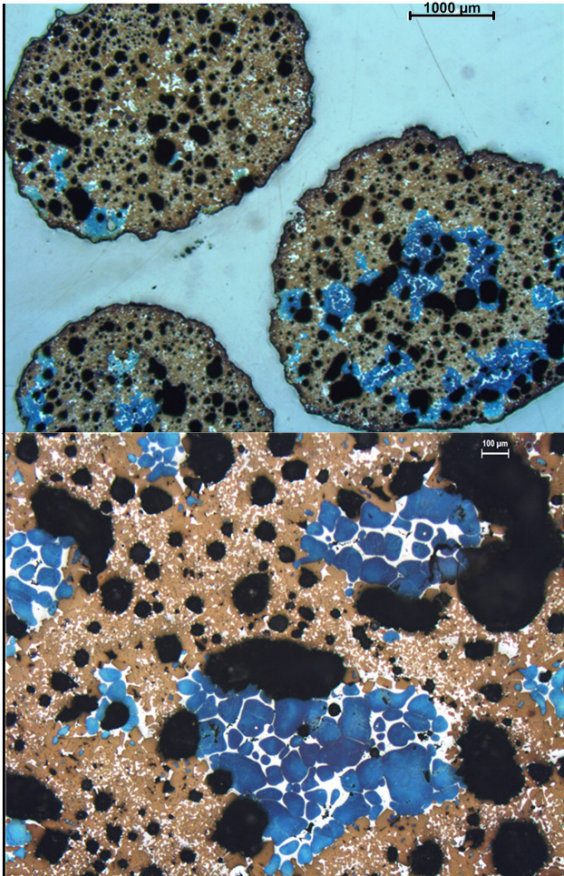


Fig. 5-4: Clinker crystal phases of sample agglomerates produced in the RKS observed by light microscopy after HF treatment. The brownish phase is C_3S , the bluish phase represents C_2S and the white area represents the crystallized clinker melt containing mostly C_3A and C_4AF . The black spots are pores.

5.2 The Influence of Heat Treatment Time on Clinker Formation

Clinker formation is a diffusion controlled process and as such dependent, among other parameters, on temperature and time. The influence of the temperature was shown in the reproducibility and repeatability tests in Chapter 4. The repeatability test including non-isothermal heating and rotational mode demonstrated that the clinker formation did not proceed as far as in the industrial process: the concentration of unreacted CaO is still fairly high (5.8 wt.%) after a typical burning time of 30 min even under the highest possible temperature conditions. Due to limitations of the setup it was not possible to increase the maximum temperature above 1540 °C in order to decrease the CaO concentration. Therefore the following experiments feature longer residence times with the goal of obtaining similar clinker phase compositions as in the industrial case.

To the best of the author's knowledge no process data on temperature profiles of the bed material in the ICRK are available in the open literature. There are however theoretical models available² suggesting potential temperature profiles (as a function of the location in the ICRK) as seen in Fig. 5-5. Though commonly used as test conditions for clinker formation tests^{3,4,5,9,10,14} an isothermal temperature profile for the ICRK is apparently an oversimplification. As a rough estimation the temperature profile in Fig. 5-5 can be approximated by a linear temperature-location profile. Assuming further that the bed material moves through the ICRK with constant rate, it will also experience a linear temperature-time profile. Thus, as a first assumption of the temperature profile experienced by the bed material inside the ICRK, the effect of different linear temperature-time profiles (~ 900 - 1540°C) was investigated under rotational conditions employing also longer residence times than those typically used in an ICRK due to aforementioned reasons.

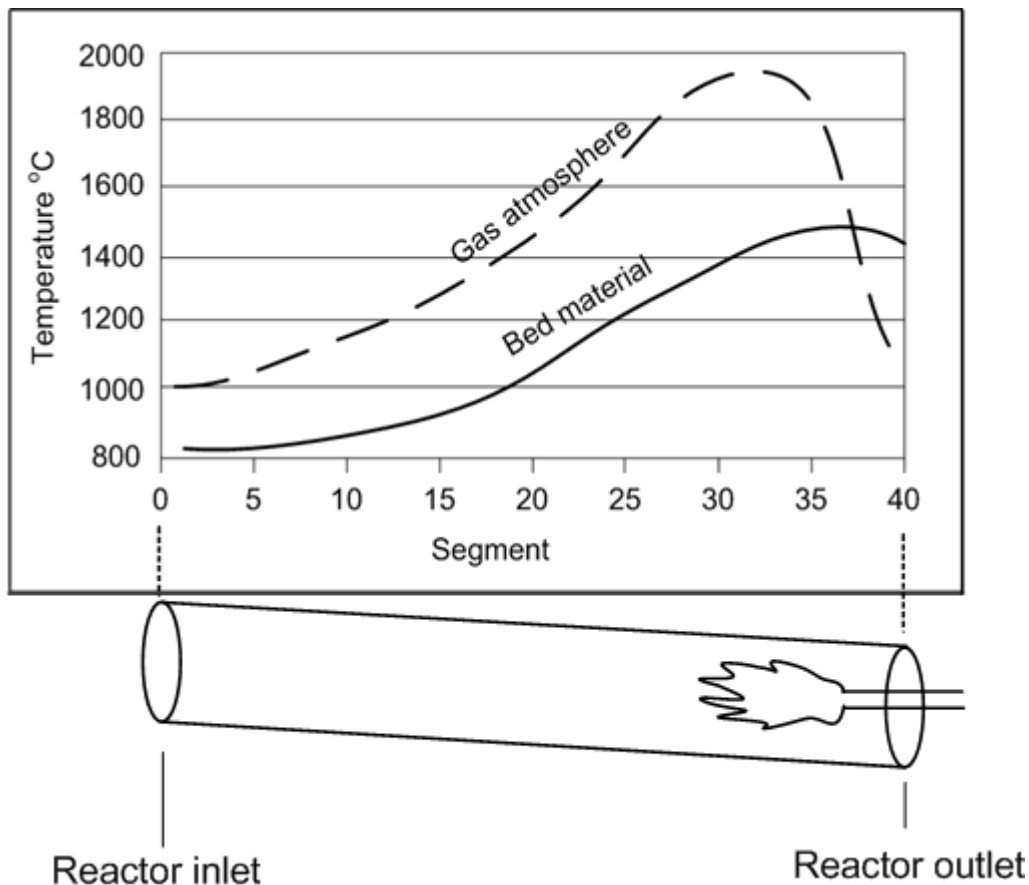


Fig. 5-5: Location-temperature profile of the bed material and the gas phase in an ICRK as calculated by Locher².

5.2.1 Experimental Procedure

A batch of ca. 450 g raw meal R (chemical composition and LSF, M_S and M_A in Tab. 5-1) was calcined at 950 °C for 45 min in a chamber oven with frequent stirring of the material. The calcined material was quickly cooled to room temperature, sieved through a 250 μm mesh to break up lumps and stored in a closed container to minimize CO_2 uptake from air. Ca. 20 g of the calcined material were inserted into the Pt/Rh-crucible, which then was placed into the SiC tube of the RKS. The heating zones of the setup furnace were all set as followed:

	Heating Zone				
	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C	1200	1300	1400	1500	1600

This resulted in a furnace gas atmosphere temperature profile from ~900-1540 °C (temperature profile 2 in Appendix B). The SiC tube with the sample was moved to ~900 °C to equilibrate the sample for 30 min and to release uptaken CO_2 from the calcined material. Next, the sample was moved through the heating furnace and heat treated at a linearized temperature-time profile (see section 3.5). Five different heat treatment times (= total residence times) were tested: 30, 45, 60, 75 and 120 min. The related velocities for each section of the temperature profile are listed in Tab. B-5 in Appendix B for each total residence time. The average heating rates are listed in Tab. 5-2. Two or three samples were burned for each heat treatment time using the average concentration for the evaluation of results (Tab. 5-2). The SiC tube was rotated with 5 rpm simultaneously to the motion along the horizontal axis. After the heat treatment, the sample was removed (within 25 sec) and cooled to room temperature with compressed air (within 2 min). The clinker samples were stored in a desiccator until sample analysis. All samples were burned under oxidizing conditions (75% N_2 and 25% O_2).

The samples were analyzed for the chemical composition (XRF) and for the clinker phase composition (XRD and Free lime analysis).

Tab. 5-1 Properties of the industrial raw meal R.

Chemical Composition in wt.%		Particle size fractions * in wt.%	
CaO	41.7	>200 μ m	1.8
SiO ₂	14.1	>125 μ m	6.5
Al ₂ O ₃	3.47	>90 μ m	12.5
Fe ₂ O ₃	2.45	>45 μ m	27.1
MgO	1.98	Acid insoluble >45 μ m	9.8
Mn ₂ O ₃	0.01	Composition of acid insoluble residue in wt.%	
TiO ₂	0.21		
P ₂ O ₅	0.02	Quartz >45 μ m Flux minerals >45 μ m Other silicates >45 μ m	
K ₂ O	0.13		
Na ₂ O	0.13		
SrO	0.03	Concentration of CaCO ₃ in >125 μ m	
Cl ⁻	0.12		
S	0.04	Unreacted CaO concentration in wt.%**	
LOI	35.8		
Clinker Moduli		Unreacted CaO concentration in wt.%**	
LSF	92	1400 °C	3.3
SR	2.4	1450 °C	1.8
AR	1.4	1500 °C	1.1

* as residues on listed sieve mesh size; ** burnability test.

Tab. 5-2 Overview and denotation of samples (Ti = time, subscript number = minutes) heat treated for different times.

	Burning time in min				
	30	45	60	75	120
Sample	Ti ₃₀	Ti ₄₅	Ti ₆₀	Ti ₇₅	Ti ₁₂₀
Average heating rate in °C/h	1296	864	648	504	324

5.2.2 Results and Discussion

The chemical composition of the sample Ti₃₀ (Tab. 5-3) is representative for all samples prepared at different total residence times. Compounds with concentrations less than 0.1 wt.% are not listed. The concentration of most oxides is similar to the concentration in the raw meal. Exceptions are Na₂O and K₂O as well as the sulfur and chloride concentrations. These form volatile compounds ^{6,7}, which are leaving the reaction system with the gas flow.

The average clinker phase compositions of samples with different heat treatment times are listed in Tab. 5-4 and the average unreacted CaO concentrations in Tab. 5-5. The development of C_3S , C_2S and unreacted CaO concentrations as a function of the total residence time is shown in Fig. 5-6.

Tab. 5-3 Representative average chemical composition and uncertainty.

Sample	Chemical composition in wt.%							
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	Na ₂ O	LOI
Ti ₃₀	66±1	22 ± 0	5.4±0.1	3.9±0.1	3.1±0.0	0.3±0.0	0.1±0.0	0.1±0.0

Tab. 5-4 Average clinker phase composition and uncertainty determined by XRD.

sample	Heat treatment time	Clinker phase concentration in wt.%						
		C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
Ti ₃₀	30 min	41 ± 3.5	29 ± 5.5	14 ± 1.8	5.3 ± 0.5	7.7 ± 0.9	1.5 ± 0.2	1.9 ± 2.9
Ti ₄₅	45 min	44 ± 0.4	27 ± 3.3	14 ± 0.4	4.3 ± 0.0	6.9 ± 1.4	1.6 ± 0.4	1.9 ± 2.7
Ti ₆₀	60 min	47 ± 0.8	23 ± 0.9	14 ± 0.5	4.6 ± 0.2	6.4 ± 6.4	1.4 ± 0.2	3.8 ± 2.8
Ti ₇₅	75 min	49 ± 2.5	23 ± 2.3	14 ± 0.8	4.5 ± 0.0	5.8 ± 1.4	1.4 ± 0.0	2.3 ± 2.7
Ti ₁₂₀	120 min	51 ± 7.5	22 ± 13.3	15 ± 4.9	4.3 ± 1.3	3.5 ± 6.5	1.3 ± 0.2	2.7 ± 12.5

Tab. 5-5 Average concentrations and uncertainties of unreacted CaO determined by Free lime analysis.

Sample	Unreacted CaO in wt.%
Ti ₃₀	5.8 ± 1.3
Ti ₄₅	4.9 ± 0.1
Ti ₆₀	4.6 ± 0.7
Ti ₇₅	4.0 ± 0.7
Ti ₁₂₀	2.7 ± 0.6

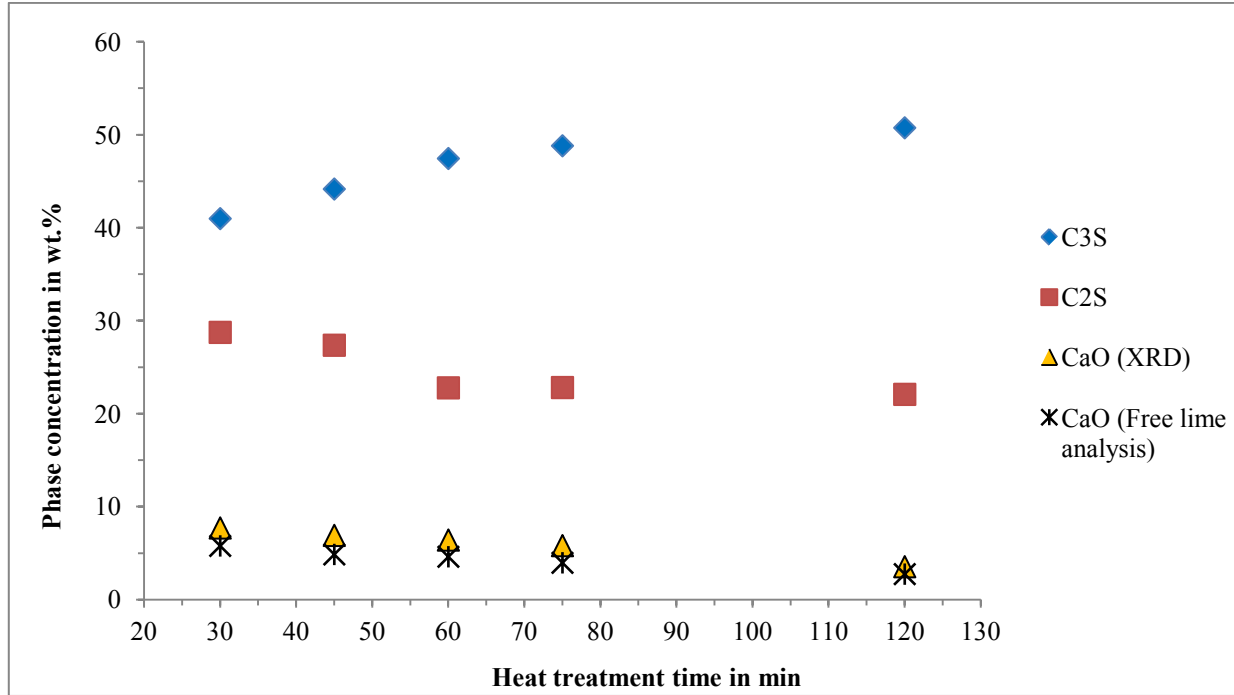


Fig. 5-6: The development of the clinker phase concentrations dependent on the heat treatment time. The C_3S concentration increases with time on the expense of the intermediate C_2S clinker phase and unreacted CaO .

Some tendencies in the development of the clinker phase concentrations can be observed. All clinker samples contain the typical clinker crystal phases: C_3S , C_2S , C_3A , C_4AF and unreacted CaO (Tab. 5-4). Additionally, free MgO (periclase) is found. MgO , often contained as carbonate (e.g. magnesite, dolomite) in the raw meal, forms periclase (free MgO) in clinker if its concentration in the calcined raw meal is not below 5 wt.%⁸. Interestingly, periclase is always found in clinker samples, although the MgO concentration in the calcined raw meal is less than 5 wt.% (it is ~3 wt.% see Tab. 5-1). The concentrations of C_3A , C_4AF and MgO remain constant in all clinker samples and are therefore, within the time interval tested, not dependent on the total residence time. The main constituent of all clinker samples is C_3S . After a residence time of 30 min (Ti_{30}) its concentration in clinker is ~41 wt.%. But the sample contains also higher concentrations of C_2S and unreacted CaO (~29 and 7.7 wt.%). At longer total residence times the C_2S and unreacted CaO concentrations are lower resulting in higher C_3S concentration. But even within the highest residence time of 120 min, the reaction of C_2S with CaO forming C_3S is not completed, which can be seen from the high concentration of unreacted CaO (~2.7 wt.%; Tab. 5-5).

The commonly accepted relationship between the total residence time and the progress of the alite formation was confirmed. The longer the residence time the lower is the unreacted CaO concentration and the higher the C_3S concentration (Fig. 5-6)^{3,5}. However, the clinker products in the RKS are not yet comparable in composition with industrial clinker. The unreacted CaO concentrations are higher than the common concentration (~1 wt.%) of industrial clinker. Furthermore, total residence times of above 1 h are beyond residence times of the bed material in an industrial cement rotary kiln. Thus, with the approximation of the temperature-location profile to be roughly linear (see introduction to subsection 5.2) the assumption of bed material movement through the reactor with a constant rate is apparently not describing the IRK correctly. Therefore, more complex non-linear heating profiles were tested, as described later in subsection 5.5. The residence time for those experiments was chosen to be 45 min, since it is somewhat typical for industrial residence times (~30-60 min). For reasons of comparability, other experiments were also carried out with a residence time of 45 min.

5.3 Stepwise Temperature Dependent Clinker Formation in the RKS

In only a few studies the temperature stepwise formation of clinker phases was (partly) conducted^{9, 10, 11}Error! Bookmark not defined.. The most detailed study was done by *in situ* synchrotron powder diffraction analysis where, however the very small amounts of material placed in a capillary did not allow the clinker to be formed in rotation mode¹¹. Another study included the rotational motion and agglomerate formation, however non-isothermal heating was only realized to a temperature of 1450 °C continuing clinker formation isothermally at this final temperature¹⁰. In the test series presented here, full non-isothermal heating until the end of the sample burning (also with a higher maximum temperature) is combined with the formation of agglomerates obtained due to rotational motion. Important steps in the clinker formation in the RKS will be discussed, forming the basis of subsequent experiments.

5.3.1 Experimental Procedure

Sample preparation and burning was conducted similar to section 5.2.1 except for the following modifications. Only three samples were heat treated over the whole temperature profile for the total residence time of 45 min. The heat treatment of the remaining samples was stopped at specific temperatures (= final temperatures), i.e. the heat treatment time was shorter as well. A list of

samples with the related final temperature and residence time is given in Tab. 5-6. Two to three samples were burned for each experimental point.

The heat treatment with low final temperatures resulted in the occurrence of additional phases, e.g. CaCO_3 , Ca(OH)_2 and SiO_2 . This caused severe overlapping of peaks in the XRD pattern of those samples (up to $T_{\text{R}}1350$), which complicated the Rietveld refinement significantly and lead to miscalculations of the concentrations, evident e.g. as a highly negative residual concentration (ca. - 15 wt.%). In order to solve the problem, the Rietveld refinement was done manually, fixing refinement parameters of individual clinker phases. The values of these parameters were obtained by an ordinary refinement of samples related to $T_{\text{R}}1540$, where peaks were automatically correlated to a clinker phase by the program. In addition to the fixation of parameters, the concentration of the internal standard was recalibrated. Here, the refinement program was used to find the concentration of TiO_2 which was added to each sample for XRD analysis. For samples heat treated to high final temperatures (e.g. 1540 °C), the concentration found by the refinement was nearly similar to the TiO_2 concentration added to the samples. At lower final temperatures, the concentration differs. This is related to the aforementioned complications of the Rietveld refinement and not to sample preparation errors. Therefore, the TiO_2 -concentrations found by the program for each sample were used to fix the TiO_2 concentration in the program thereafter in order to calculate the concentrations of the remaining clinker phases. This results in the removal of the negative residual and repeatable clinker phase concentrations of the samples prepared under the same experimental conditions. Within this test series, reasonable tendencies of the development of the clinker phases depending on the final temperature, useful for phenomenological description of clinker formation in the RKS, were obtained. Note however that the absolute concentration values cannot be compared with other test series, due to the specific XRD refinement procedure.

Tab. 5-6 List of samples related to the final temperature of the heat treatment and the corresponding residence time.

Sample	Final temperature in °C	Residence time in h
T _R 900	900	0
T _R 1000	1000	0.11
T _R 1100	1100	0.23
T _R 1200	1200	0.36
T _R 1300	1300	0.47
T _R 1350	1350	0.52
T _R 1400	1400	0.58
T _R 1450	1450	0.63
T _R 1500	1500	0.70
T _R 1540	1540	0.74

5.3.2 Results and Discussion

The chemical compositions of samples heat treated to a final temperature ≥ 1200 °C are listed in Tab. 5-7. Compounds of concentrations <0.1 wt.% are not listed. The concentrations of the main oxides deviate slightly, which could be either due to deviations in the raw meal- and/or clinker sample homogeneity or to analysis uncertainties. These fluctuations result in a higher uncertainty of the average LSF, which is listed together with the M_S and M_A in Tab. 5-8. A decrease in the volatile compounds (K_2O , Na_2O and SO_3) with increasing temperature can be observed. As discussed in previously, these compounds are released from the bed material and carried out of the reaction vessel due to the co-current gas flow.

Tab. 5-7 Representative chemical compositions.

Sample	Chemical composition in wt.%									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	K ₂ O	Na ₂ O	SO ₃	LOI
T _R 1200	64	22	5.4	3.8	3.0	0.3	0.2	0.2	0.1	0.3
T _R 1300	65	22	5.4	3.9	3.1	0.3	0.1	0.2	0.1	0.7
T _R 1350	65	22	5.4	3.9	3.1	0.3	0.1	0.2	0.1	0.4
T _R 1400	66	21	5.4	3.9	3.1	0.3	0.0	0.1	0.0	0.3
T _R 1450	66	22	5.5	3.9	3.1	0.3	0.0	0.2	0.0	0.2
T _R 1500	66	21	5.5	4.0	3.1	0.3	0.0	0.1	0.0	0.2
T _R 1540	66	22	5.4	3.9	3.1	0.3	0.0	0.1	0.0	0.2

Tab. 5-8 Average LSF, M_S and M_A .

LSF	M_S	M_A
94 ± 4	2.3 ± 0.1	1.4 ± 0.0

The average phase concentrations of clinker as effect of the final temperature of the heat treatment are listed in Tab. 5-9 and shown in Fig. 5-7. The tendencies observed for the phase concentrations in clinker samples prepared in the new setup in rotational mode agree well with the literature on clinker phase formation obtained from experiments conducted with preformed agglomerates (of various shapes) ^{5,9,27}. The main constituents at low temperatures (T_{R900} and T_{R1000}) are unreacted CaO and quartz. C_2S and C_3A were also already formed in low concentrations, which is in good agreement with what is known of clinker formation in the industrial process, where e.g. C_2S formation can already occur in the pre-calcliner. Periclase is also present in clinker. Despite these phases, intermediate clinker phases as for example $C_{12}A_7$ were not found. The concentration of C_4AF fluctuates at the low temperatures (T_{R900} - T_{R1200}) between 0 and 2 wt.% and its presence at these low temperatures is doubtful and may be an artifact from XRD analysis. C_4AF forms dark colored crystals ¹², which are responsible for the color of gray cement. The clinker samples heat treated up to 1200 °C show only light brownish color (Fig. 5-8), indicating the absence of C_4AF . The formation of the crystal phase is observable by the onset of color change at 1300 °C (T_{R1300}) shown in Fig. 5-8. The C_2S , C_3A and C_4AF concentrations increase with increasing heat treatment temperatures (e.g. at 1350 °C i.e. sample T_{R1350}), whereas the unreacted CaO and quartz concentrations decrease due to the consumption in the formation of the calcium silicate phases. The strong increase of C_3S concentration, but also the starting change of color ¹⁰, are indicators of the temperature range of melt formation, which is considered to start at ~1300 °C in small amounts but increases significantly at 1350-1400 °C. Besides the continuous formation of C_2S , the C_3S formation starts. Quartz is completely consumed at approximately 1400 °C (T_{R1400}) and the C_2S formation reaches its maximum as well as the C_3A and C_4AF formation. Often it is assumed, that quartz has already completely reacted forming clinker silicate phase at temperatures above 1300 °C ¹³, which is in contrast to the finding of the clinker formation from raw meal R in the RKS. However, the constant C_2S formation, which is only possible in presence of SiO_2 source, until ~ 1400 °C, points out, that quartz is truly present in the clinker samples T_{R900} - T_{R1350} .

As the concentration of C_3S increases, the concentration of unreacted CaO decreases. Within the first interval, the C_3S formation consumed C_2S as well. But since the C_2S concentration remained

nearly constant it is assumed, that unreacted CaO was still reacting with siliceous compounds forming C₂S simultaneously to its consumption. Further development of the clinker formation is characterized by the increase of C₃S and the consumption of C₂S and unreacted CaO. Clinker samples (T_R1540) prepared with the final temperature of 1540 °C still show a rather high unreacted CaO concentration.

Tab. 5-9 Average clinker phase composition and uncertainty determined by XRD.

Samples	Clinker phase concentration in wt. %						
	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	MgO	CaO	Quartz
T _R 900	0.0 ± 0.0	8.5 ± 2.9	1.9 ± 5.9	3.9 ± 1.4	2.6 ± 0.2	64 ± 4	19 ± 2
T _R 1000	0.0 ± 0.0	13 ± 8	0.0 ± 0.0	4.0 ± 1.9	2.6 ± 0.5	62 ± 8	19 ± 3
T _R 1100	0.0 ± 0.0	21 ± 2	1.5 ± 1.3	4.3 ± 0.5	2.5 ± 0.2	55 ± 1	15 ± 3
T _R 1200	0.0 ± 0.0	20 ± 7	0.0 ± 0.0	3.1 ± 0.5	2.5 ± 0.3	58 ± 5	17 ± 1
T _R 1300	0.0 ± 0.0	37 ± 2	1.7 ± 1.3	3.5 ± 0.9	2.4 ± 0.0	47 ± 2	8.6 ± 1.3
T _R 1350	4.5 ± 12.7	36 ± 9	4.5 ± 2.7	4.3 ± 3.9	2.1 ± 0.8	41 ± 16	7.3 ± 8.9
T _R 1400	25 ± 5	37 ± 1	14 ± 1	5.9 ± 2.3	1.7 ± 0.1	16 ± 4	0.0 ± 0.0
T _R 1450	30 ± 1	38 ± 0	14 ± 0	4.8 ± 0.1	1.5 ± 0.1	12 ± 1	0.0 ± 0.0
T _R 1500	42 ± 2	28 ± 3	15 ± 0	4.8 ± 0.7	1.5 ± 0.3	8.8 ± 0.9	0.0 ± 0.0
T _R 1540	47 ± 3	25 ± 4	15 ± 1	4.8 ± 0.6	1.4 ± 0.1	7.2 ± 0.6	0.0 ± 0.0

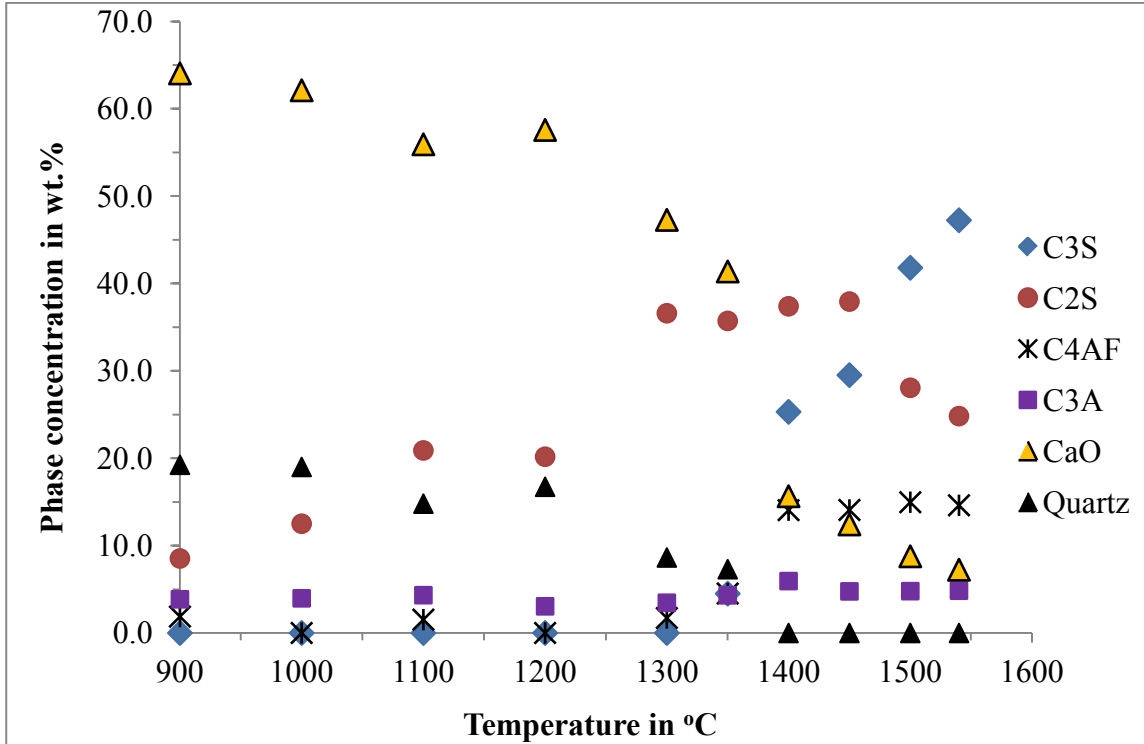


Fig. 5-7: Clinker phase development dependent of the heat treatment temperature.

The clinker phase formation in the RKS could be divided into 2-3 main steps, which is in good agreement with what was observed by others^{9,10,11}. The first step is the formation of the aluminate phases and the C_2S phase at 900-1350 °C, the second step the formation of melt at ~1350-1400 °C and the third step the formation of C_3S at the expense of CaO and C_2S at temperatures >1400 °C. The last two steps are overlapping and might be considered as one. Although these tendencies are also observed by De la Torre *et al.*¹¹ and Maas *et al.*¹⁰, the temperature ranges, where these steps occur, differ. The melt and C_3S formation were reported to start already at ~1230 °C¹¹ in the former case and in the latter case at ~1200-1300 °C¹⁰. Contrary to the observations by Maas *et al.*, the C_3S formation in the RKS starts already before the C_2S formation was finished. That means that the CaO diffusion in the Raw meal R is apparently slower than in the raw meals used by Maas *et al.*, since the CaO has not reacted with all the available siliceous compounds forming C_2S before the temperature of ~1250 °C (where C_3S is thermodynamically stable) was reached. This outlines the differences in clinker formation in different raw meals, although the fundamental steps are comparable.

Besides the clinker phase formation, agglomerate formation up to a final temperature of 1300 °C was evaluated. As shown in Fig. 5-8, agglomeration occurs already at early stages of the heat treatment process in the RKS. Even at the first stage, i.e. the heat treatment of the calcined raw meal at 900 °C, small agglomerates were formed (Fig. 5-8a). These are very brittle and held together mostly by electrostatic forces between the powder particles, which was generally observed for calcined raw meal during sample preparation before clinker burning. The agglomerates increase in number and size and additionally the shape is more spherical with increasing temperature. Fig. 5-8b shows agglomerates formed at a maximum temperature of 1000 °C. The surface of the agglomerates is partly covered with powdery particles suggesting that also here the formation of agglomerates is mainly due to electrostatic charges than due to the occurrence of some early melt (which, however, could result from e.g. alkali sulfates; see low concentrations in Tab. 5-7). Considerable amounts of powdery materials are still present at that stage. This changes with increasing temperature. The surface of agglomerates formed at temperatures up to 1200 °C becomes smoother, which can be related to sintering of particles, but also to the formation of small amounts of melt (Fig. 5-8c). At 1300°C, no powdery parts were observed (Fig. 5-8d). The entire material formed spherical agglomerates of a broad size distribution (~0.125 mm - above 4 mm). Further size growth occurs by sintering of agglomerates, either by sintering of agglomerates of the same size or small agglomerates onto bigger ones (Fig. 5-9). Furthermore, a color change was observed. The agglomerates show black spots, due to formation of C_4AF , outlining regional differences of the chemical composition and probably different progress of phase formation. The early formation of agglomerates might affect the homogeneity of the bed material in the RKS. The alignment of the powder in agglomerates, which become stronger with increasing temperature, reduces the mixing of the material. At low temperature (ca. 900-1100 °C) the powder agglomerates probably collapse partly, facilitating mixing. With higher temperatures (but still below the formation of melt), the mixing effect decreases. This may signify a severe difference to the industrial process. Here, the pressure of the bed material might crush all weak agglomerates in the bed volume, sustaining proper mixing until agglomerates due to melt formation occur. Thus, high sample homogeneity is even more important in the RKS than in the ICRK.

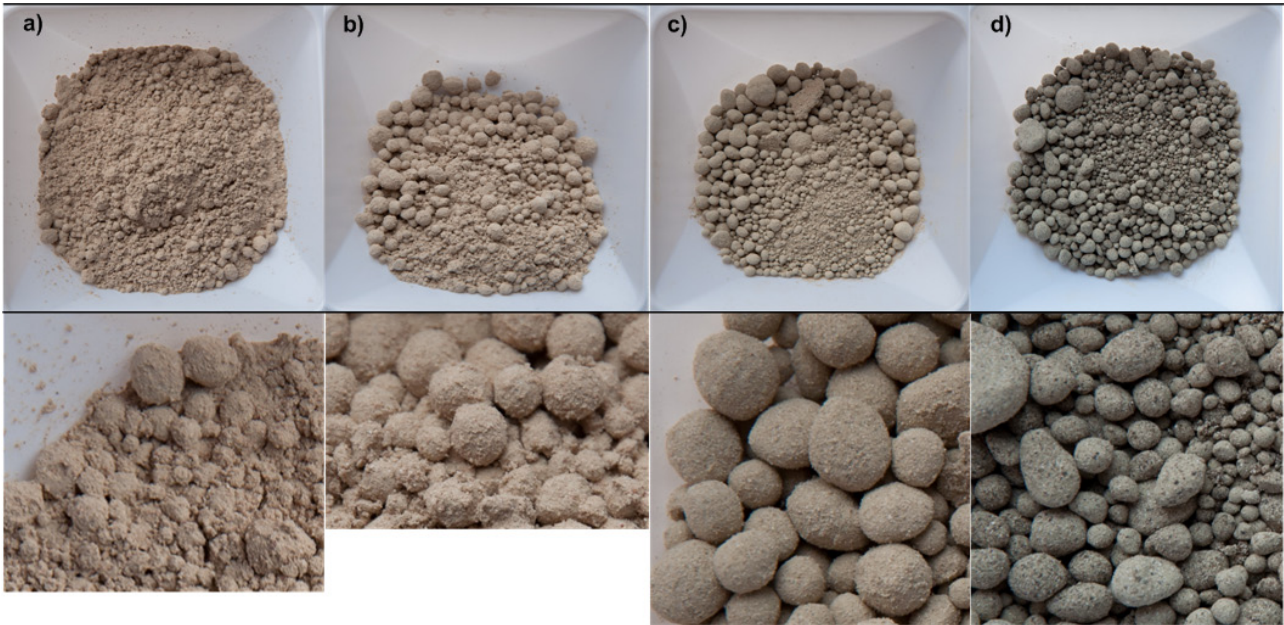


Fig. 5-8: Development of clinker agglomerates until: a) 900 °C; b) 1000 °C; c) 1200 °C and d) 1300 °C.



Fig. 5-9: Agglomerate growth by agglomeration of granules of similar size (left) and by sintering of small agglomerates onto bigger ones (right).

5.3.3 Kinetic Model

A simple kinetic model was developed on the basis of the temperature stepwise clinker formation. Most kinetic models have been developed for isothermal clinker formation^{9,14}, which has limited use adapted for non-isothermal clinker formation. Kinetic data from non-isothermal clinker burning experiments with a linear heating gradient were obtained by Imlach¹⁵. Although this approach gave satisfactory results for the decarboxylation of CaCO_3 , the degree of clinker formation by means of CaO consumption resulted in unreasonably low or even negative activation energies.

The activation energy E_a and Arrhenius parameter A for linear temperature gradients can be calculated according to Eq. 1¹⁶:

$$g(\alpha) = \frac{A}{b} \int_{T_0}^T \exp\left(-\frac{E_a}{RT}\right) dT \quad (\text{Eq. 1})$$

where b is the (linear) heating rate, T the temperature, T_0 the starting temperature at which the reaction rate is assumed to be 0, R the universal gas constant and $g(\alpha)$ the integrated rate equation as a function of the conversion α . The integral can be approximated according to¹⁶ and¹⁷ as shown in Eq. 2 (substituting $x = E_a/RT$):

$$\int_{T_0}^T \exp(-x) dT = \frac{E_a}{R} \frac{\exp(-x)}{x^2} Q(x) \quad (\text{Eq. 2})$$

with $Q(x)$:

$$Q(x) = \frac{x^4 + 18x^3 + 86x^2 + 96x}{x^4 + 20x^3 + 120x^2 + 240x + 120} \quad (\text{Eq. 3})$$

An integrated rate law for the formation of alite from CaO can be found in⁹:

$$(1 - \sqrt[3]{1 - \alpha})^2 = g(\alpha) \quad (\text{Eq. 4})$$

The conversion α can be defined based on the conversion of free CaO¹⁶, based on the formation of alite⁹ or the arithmetic mean of both as recommended by⁹. A kinetic analysis of clinker formation was derived from all three definitions shown in Eq. 5a-c.

$$\alpha_{CaO} = \frac{c_{CaO,0} - c_{CaO}}{c_{CaO,0}} \quad (\text{Eq. 5a})$$

$$\alpha_{alite} = \frac{c_{alite}}{c_{alite,max}} \quad (\text{Eq. 5b})$$

$$\alpha_{mix} = \frac{\alpha_{CaO} + \alpha_{alite}}{2} \quad (\text{Eq. 5c})$$

with c_{CaO} as the concentration of free CaO for a specific sample, $c_{CaO,0}$ as the concentration of free CaO of the unreacted raw meal, c_{alite} as the concentration of alite for a specific sample and $c_{alite,max}$

as the maximum concentration of alite in the sample, which was calculated from the Bogue equation (see chapter 2). Eq.1 in combination with Eq. 2 can be linearized resulting in Eq. 6:

$$\ln\left(\frac{g(\alpha)}{Q(x)T^2}\right) = \ln\left(\frac{AR}{bE_a}\right) - \frac{E_a}{RT} \quad (\text{Eq. 6})$$

Thus from a linear plot the Arrhenius parameter can be calculated from the intercept and the activation energy from the slope. Since E_a is necessary to calculate $Q(x)$, it was obtained iteratively with a starting value of 200 kJ/mol. Eq. 6 gives a reasonably linear plot for temperatures $>1350^\circ\text{C}$ which is where noticeable alite formation occurs. Fig. 5-10 shows the plot for using α_{mix} .

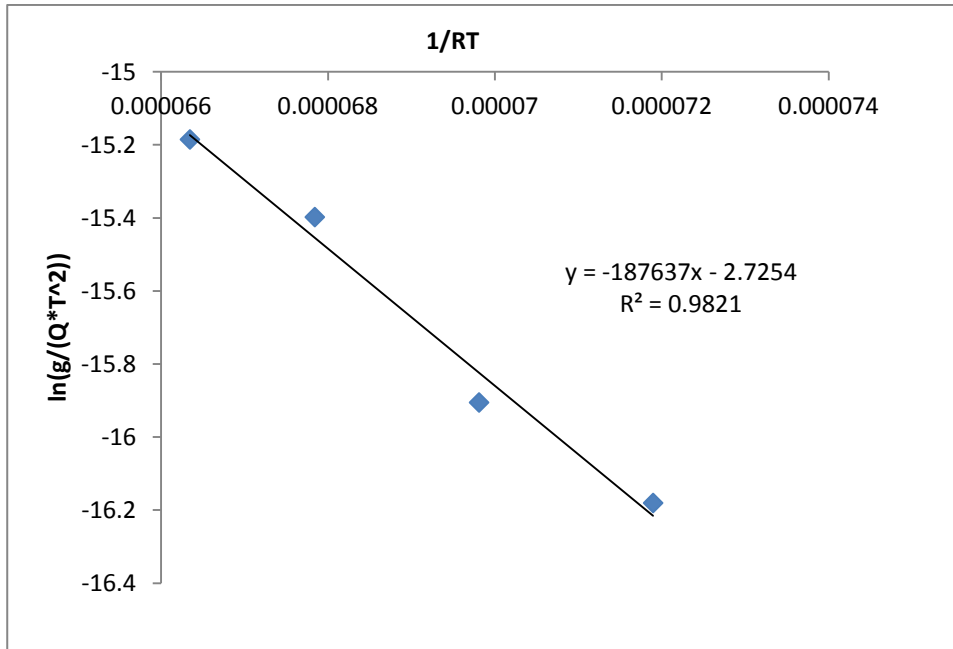


Fig 5-10: Linear plot according to Eq. 5 for samples with final temperature 1400, 1450, 1500 and 1540 °C derived with α_{mix} .

Tab. 5-10 lists the calculated apparent activation energy E_a and the Arrhenius parameter for the three different conversions α_{CaO} , α_{alite} and α_{mix} . The apparent activation energy derived from α_{alite} and α_{mix} are in good agreement with literature data obtained from isothermal studies^{9,14} which are often in the range of 200 - 500 kJ/mol.

Table 5-10 Activation energies and Arrhenius parameters obtained with different definitions of the conversion α .

	α_{CaO}	α_{alite}	α_{mix}
E_a (kJ/mol)	86	311	188
A (h^{-1})	840	5.7×10^9	1.3×10^6

The results of the experiments on the influence of the residence time on clinker formation (subsection 5.2) were used to verify the kinetic model. Here, Eq. 6 and Eq. 4 were used to calculate the conversion α_{model} for all five residence times, i.e. at final temperature of 1540 °C. α_{mix} (model) is compared to the experimentally obtained conversions α_{exp} . The samples, the related heating rates and conversions related are listed in Tab. 5-11. Fig. 5-11 shows the comparison of both conversions. A relatively good correlation between the experimental and model conversion is found, given the fact of the relatively high experimental uncertainties and the simplicity of the model. There is, however, still a systematic deviation between model and experiment. It can be observed, that at lower heating rates the model conversion is systematically overestimated. Apparently, a parameter influencing the clinker formation is not comprised by the model. The nature of this parameter can only be speculated. It might correlate to increasing diffusion limitations due to crystal size growth occurring at lower temperatures to a greater extent at longer residence times, since the model does only comprehend changes in alite and CaO concentrations but not the microstructural starting conditions. Nevertheless, the model presents a useful tool, allowing prediction an approximate alite and unreacted CaO concentration for linear heat treatment at temperatures between 1400 – 1540 °C.

Tab. 5-11 The experimental and model conversion factors for time dependent clinker phase formation experiment samples of subsection 5.2).

Sample	Heating rate (°C/h)	α_{exp}	α_{model}
Ti ₃₀	1007	0.78	0.75
Ti ₄₅	577	0.81	0.84
Ti ₆₀	367	0.84	0.89
Ti ₇₅	237	0.86	0.93
Ti ₁₂₀	47	0.90	0.98

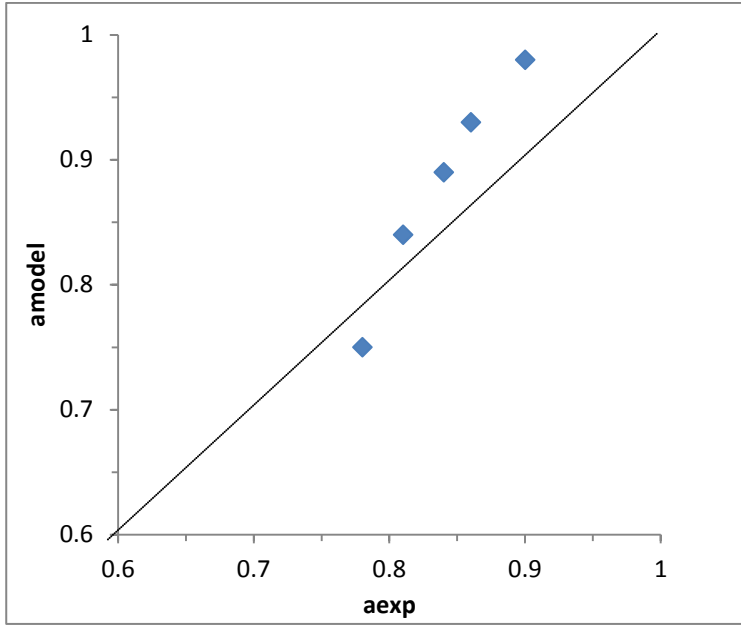


Fig. 5-11: The correlation of the conversion factors α_{exp} and α_{model} .

5.4 The Influence of the Rotation Velocity on Clinker Formation

The rotation of the industrial cement kiln causes movement of the bed material around the horizontal axis and, including the inclination of the kiln, along the horizontal axis. The motion of the bed materials results in the formation of relatively spherical agglomerates. Granulation studies have mostly been carried out in rotating drums at room temperature using granulated material^{18,19,20,21}. Water added to the granules, constituted the liquid phase, which is important for the formation of agglomerates. As already mentioned Maas *et al.*¹⁰ investigated clinker formation including the rotation motion. But, a study on the influence of rotation velocity on clinker formation was not conducted. This was done in the following experiments. Here, 3 rotation velocities, i.e. 5, 15 and 25 rpm, were chosen. The related Froude numbers are listed in Tab. 5-12, which are typical for rolling motion of bed material in a rotary kiln¹⁸. However, these numbers are smaller compared to the Froude number of the industrial rotary kiln, i.e. the RKS should be rotated faster than 25 rpm. This was not possible due to the limitations of the used step motor. Nevertheless, the rolling motion was observed in pretests, which is the important basis of granulation test and it is assumed that tendencies are similar at higher rotation velocities, as long as the material is not changing to cascading motion.

Tab. 5-12 The rotation velocities in the RKS and in the ICRK and the corresponding Froude numbers.

Reactor	rpm	Froude number
RKS	5	0.001
RKS	15	0.005
RKS	25	0.015
ICRK	3.7	0.035

5.4.1 Experimental Procedure

In this investigation a new raw meal was used, which is denoted in the following as raw meal Q. This cement plant uses coal as burner fuel, in the rotary kiln. Therefore, coal received from the cement plant was combusted and the ash mixed together with calcined the raw meal. The preparation of the ash and the calculation of amount needed to admix with the raw meal were carried out at the laboratories of FLSmidth in Dania. The chemical composition of the raw meal with and without admixed ash, the LSF, M_S and M_A , the particle size fractions und the unreacted CaO concentrations at different temperatures are listed in Tab. 5-13. A batch of ca. 550 g was divided into two parts and each was calcined at 950 °C for 45 min in a chamber oven with frequent stirring of the material. The calcined material was quickly cooled to room temperature and both parts were combined. 1.2 wt.% of coal ash (calculated for the uncalcined raw meal) was added and the mixture was sieved through a 250 µm mesh to break up lumps. Thereafter, the material was mixed again for 15 min. The heat treatment of samples was conducted similar to subsection 5.2.1 except for the following changes. After the equilibration of the samples at ~900 °C for 30 min, the material was moved through the heating furnace using the linear heating profile from ~900-1540 °C. The related heating rates are listed in Tab. B-13 and B-14 (Appendix B). The heat treatment of a sample was stopped either at 1300, 1450 or 1500°C (= final temperature). In this way the influence of the rotation velocity on clinker formation was studied temperature stepwise. Three different rotation velocities were chosen: 5, 15 and 25 rpm. The samples are listed in Tab. 5-14.

Additionally, four calcined samples were heat treated till 1300 °C, two samples at 5 rpm and two samples at 15 rpm rotation velocity. The formed agglomerates of one sample were separated from the lining, and each fraction was combined with the agglomerates and lining fraction, respectively, of the second sample prepared under exactly the same experimental conditions were combined. The fractions were analyzed by XRD and XRF.

The physical appearance of the clinker formed in the RKS can be divided into spherical clinker agglomerates and lining. The combined lining and agglomerate fractions of each sample were evaluated for the agglomerate size distribution by sieving. The lining consisted mainly of weakly held together agglomerates and therefor broke up into these agglomerates during sieving. The agglomerate sizes were divided into three fractions: a fraction of agglomerates with diameter > 2 mm, a fraction from 1-2 mm in diameter and a fraction of < 1 mm in diameter.

Tab. 5-13 The raw meal properties of cement raw meal Q.

Chemical Composition in wt.%		Particle size fractions* in wt.%	
CaO	42.3	>200µm	0.9
SiO ₂	14.1	>125µm	3.7
Al ₂ O ₃	3.52	>90µm	9.8
Fe ₂ O ₃	2.01	>45µm	25.1
MgO	1.32	Acid insoluble >45µm	9.8
TiO ₂	0.19	Composition of acid insoluble residue in wt.%	
P ₂ O ₅	0.10		
K ₂ O	0.46		
Na ₂ O	0.16		
Cl ⁻	0.02	Quartz >45µm	0.89
S	0.20	Flux minerals >45µm	0.22
LOI	35.8	Other silicates >45µm	2.29
		Concentration of CaCO ₃ in >125µm	2.45
Clinker Moduli		Unreacted CaO concentration in wt.%**	
LSF	94	1400 °C	2.2
M _S	2.6	1450 °C	1.5
M _A	1.8	1500 °C	1.2

* as residues on listed sieve mesh size; ** burnability test.

Tab. 5-14 Sample denotation: V= rotational Velocity, Q=raw meal Q, A=Agglomerates, L= Lining.

Sample	Final temperature in °C	Rotation velocity in rpm
V5 _Q 1300	1300	5
V15 _Q 1300	1300	15
V25 _Q 1300	1300	25
V5 _Q 1450	1450	5
V15 _Q 1450	1450	15
V25 _Q 1450	1450	25
V5 _Q 1500	1500	5
V15 _Q 1500	1500	15
V25 _Q 1500	1500	25
V5 _Q A	1300	5
V5 _Q L	1300	5
V15 _Q A	1300	15
V15 _Q L	1300	15

5.4.2 Results and Discussion

Representative average clinker phase concentrations and chemical compositions of samples prepared with 5 rpm rotation velocity (one with 15 rpm for comparison) and with the final temperature of 1300, 1450 and 1500 °C are listed in Tab. 5-15 - Tab. 5-17, latter including also the related LSF, M_s and M_A . As discussed before clinker formation increases with the temperature. The clinker phase composition in this test series differs only with the change of the final temperature, but is not affected by the rotation velocity (V5_Q1450 and V15_Q1450), which was found as a general tendency (Tab. C-4 appendix C). As observed previously the main difference in the chemical composition of the samples with increasing temperature is the concentration of K₂O and sulfur (here denoted as SO₃). The rotation velocity does not influence the chemical composition (V5_Q1450 and V15_Q1450).

Tab. 5-15 Average clinker phase composition and uncertainty determined by XRD.

		Clinker phase concentration in wt.%						
Sample	rpm	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	MgO	CaO	Residual
V5 _Q 1300	5	4.6 ± 1.2	58 ± 0.2	6.6 ± 0.7	3.6 ± 0.1	1.0 ± 0.2	23 ± 0.3	-3.4 ± 2.1
V5 _Q 1450	5	30 ± 2.4	49 ± 1.5	11 ± 3	6.1 ± 1.0	0.7 ± 0.2	8.2 ± 9.7	-8.3 ± 2.6
V15 _Q 1450	15	29 ± 0	48 ± 4	11 ± 5	5.9 ± 0.6	0.6 ± 0.3	7.3 ± 8.2	-4.4 ± 0.3
V5 _Q 1500	5	41 ± 5.4	38 ± 11.6	11 ± 1	5.2 ± 0.6	0.6 ± 0.3	7.1 ± 4.3	-4.4 ± 10.8

Tab. 5-16 Average unreacted CaO concentration and uncertainty determined by Free lime analysis.

Sample	Unreacted CaO in wt. %
V5 _Q 1300	18 ± 0
V5 _Q 1450	7.3 ± 0.4
V5 _Q 1500	5.0 ± 2.0

Tab. 5-17 Representative average chemical composition and uncertainty.

	Chemical composition in wt. %			
	V5 _Q 1300	V5 _Q 1450	V15 _Q 1450	V5 _Q 1500
CaO	65 ± 0	66 ± 1	66 ± 0	66 ± 1
SiO ₂	22 ± 0.2	22 ± 0.2	22 ± 0	22 ± 0.2
Al ₂ O ₃	5.4 ± 0.1	5.5 ± 0.0	5.5 ± 0.0	5.5 ± 0.1
Fe ₂ O ₃	3.1 ± 0.0	3.1 ± 0.0	3.1 ± 0.0	3.2 ± 0.0
MgO	2.0 ± 0.0	2.0 ± 0.0	2.0 ± 0.0	2.0 ± 0.0
TiO ₂	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.3 ± 0.0
P ₂ O ₅	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.0 ± 0.0
K ₂ O	0.6 ± 0.0	0.3 ± 0.0	0.3 ± 0.0	0.2 ± 0.0
Na ₂ O	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0	0.2 ± 0.0
SO ₃	0.7 ± 0.0	0.4 ± 0.0	0.4 ± 0.0	0.2 ± 0.0
LOI	1.0 ± 0.4	0.7 ± 0.8	0.4 ± 0.1	0.7 ± 0.5
LSF	94 ± 0.0	94 ± 0.0	94 ± 0.0	94 ± 0.0
M _S	2.6 ± 0.1	2.5 ± 0.0	2.5 ± 0.0	2.5 ± 0.0
M _A	1.8 ± 0.1	1.8 ± 0.1	1.8 ± 0.0	1.8 ± 0.1

The average amounts of the agglomerate size fractions are shown in Fig. 5-13 (listed in Tab. C-5 - Tab. C-7 in Appendix C). Samples treated with the same rotation velocity where the heat treatment was stopped at different final temperatures (V5_Q1300, V5_Q1450 and V5_Q1500) show a slight increase of the >2 mm size fraction and a decrease of the size fraction <1 mm with an increase of the final temperature. However, the difference in the relative amounts of a size fraction (e.g. > 2 mm) for the different final temperatures is small indicating that strong agglomerates are already formed at lower temperatures, i.e. 1300 °C. This is probably due to an early melt formation, i.e. below 1300 °C, which is in contrast to melt formation of the raw meal R (subsection 6.3). Fig. 5-12 shows parts of the clinker product obtained for different final temperatures and rotations velocities: Fig. 5-12a-c shows V5_Q1300- V25_Q1300, Fig. 5-12d-f samples V5_Q1450- V25_Q1450 and Fig. 5-12g-i samples V5_Q1500- V25_Q1500. Sample heat treated till the final temperature of 1300°C show

light yellowish-brownish agglomerates, but also dark and black ones. The change of the color to black is related to the formation of C_4AF and potential clinker melt (as discussed before)¹⁰. These clinker samples from raw meal Q consist of more dark nodules than the comparable raw meal R sample T_R1300 (Fig. 5-8). This indicates the earlier formation of clinker melt in former samples.

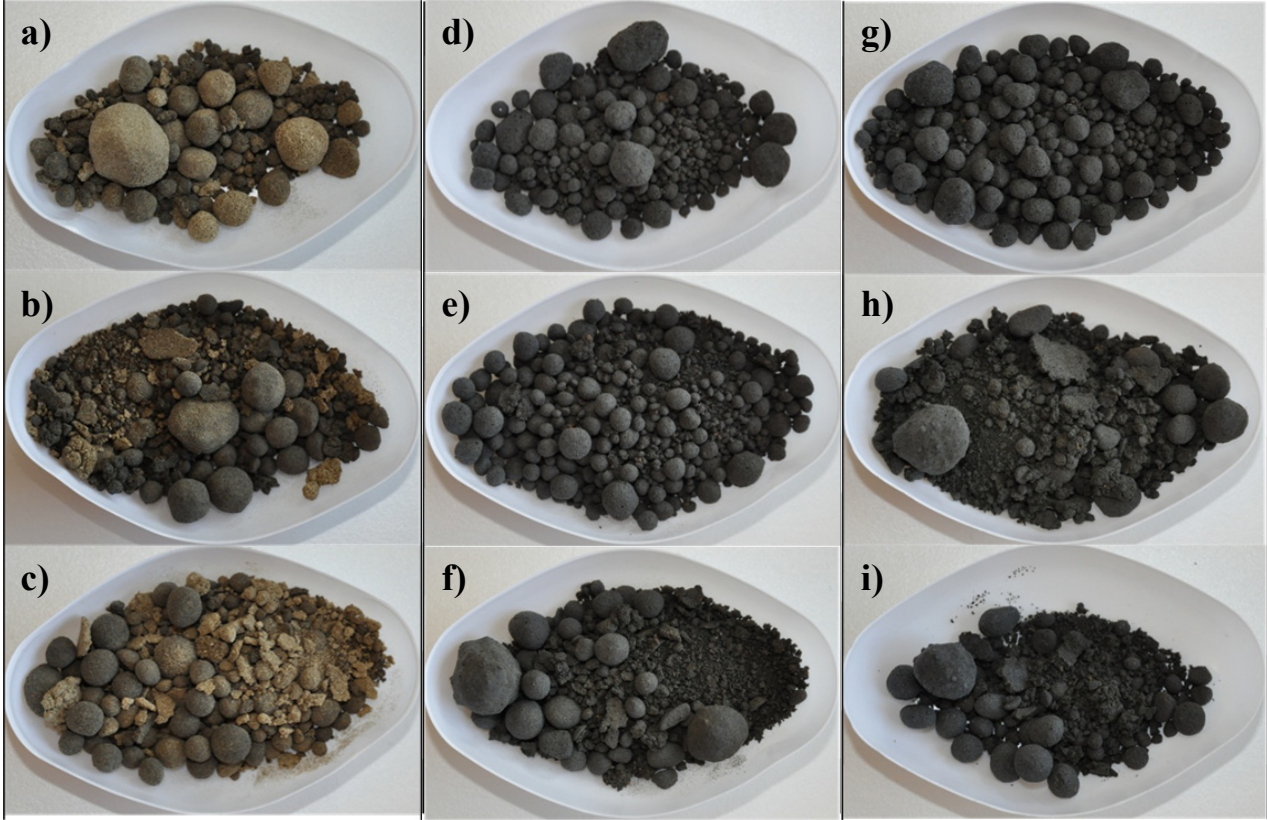


Fig. 5-12: Agglomerate development dependent on the final temperature of the heat treatment and on the rotation velocity: a-c) final temperature 1300 °C rotation velocity 5, 15 and 25; d-f) final temperature 1450 °C rotation velocity 5, 15 and 25; g-i) final temperature 1500 °C rotation velocity 5, 15 and 25.

As previously described (subsection 5.3), the formation of agglomerates occurs by coalescence of particles and agglomerates. This is influenced by the rotation velocity, since the relative amount of smaller particles increases with increasing velocity. Fig. 5-13 shows the relative amount of the three agglomerate size fractions as function of the rotation velocity. Regardless of the final temperature, the agglomerate size fraction >2 mm decreases significantly with increasing the rotation velocity from 5 to 15 or 25 rpm, whereas the smallest fraction, <1 mm, increases. The amount of the middle fraction remains nearly constant in concentration. The mean particle size decreases from 1-2 mm to

0.5-1 mm in case of sample heat treated to 1300°C or from 2-4 mm to 0.5-1mm (for 1450 °C) and 2-4 mm to 1-2 mm in case of the 1500 °C final temperature. The effect of the rotation velocity on the agglomerate size is twofold. It defines the time available for particles to adhere to each other while they are rolling, and it increases the number of particle collisions thus breaking weakly bound agglomerates^{19,20}.

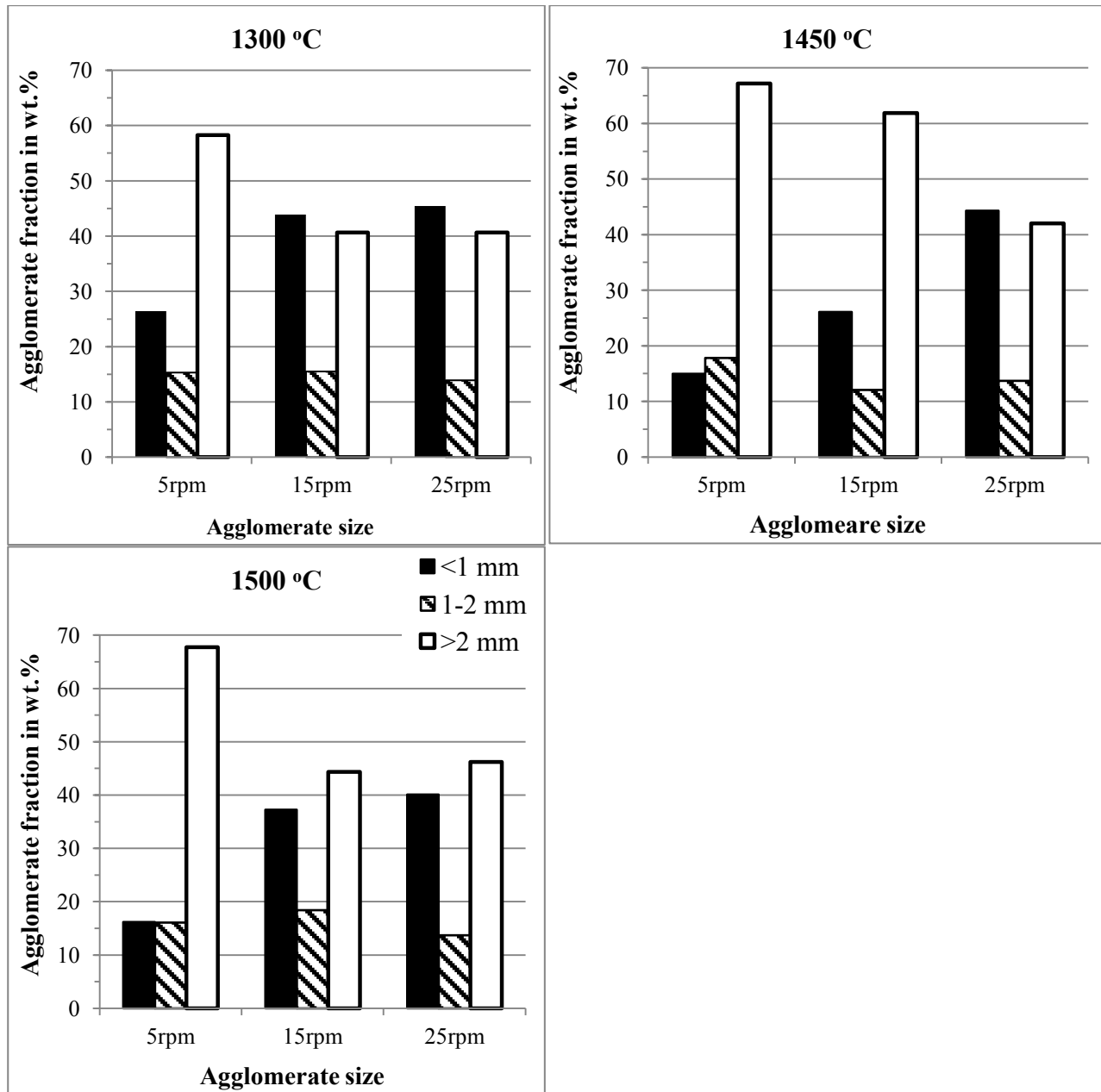


Fig. 5-13: Particle size distribution of agglomerates dependent on the heat treatment final temperature (1300, 1450 and 1500 °C) and rotation velocity.

With increasing torque the time of contact between particles/agglomerates decreases resulting in the formation of more small agglomerates below 1 mm in diameter, which is discussed shortly in the following. As discussed in subsection 5.3 within the temperature range of 900-1100°C the agglomeration is mainly due to electrostatic charges between particles, i.e. these agglomerates grow in size by taking up small powder particles (like avalanches). The size is probably limited (≤ 4 mm maximum at 5rpm; estimated from agglomerate sizes in Fig. 5-8b), since the agglomerates also collapse due to the weak cohesion between the particles. As soon as melt formation sets in the agglomerates become stronger. The size growth occurs on one hand still by uptake of smaller powdery particles and on the other hand by agglomeration and sintering of granules. When sufficient melt is formed ($\sim 1300^\circ\text{C}$ Fig. 5-8d) no powdery residue remains. The further growth occurs only by bonding and sintering of already formed agglomerates, either of the same or different size. It could be assumed, that the rotation velocity influences mainly the growth via bonding/sintering of already formed agglomerates. The higher fraction of small agglomerates with higher rotational velocity is due to the shorter time which the agglomerates have to anneal in general. Furthermore, it is fair to assume that weakly electrostatically bound agglomerates are smaller in size at the higher rotation, due to a higher collapsing rate. Therefore, the concentration of smaller agglomerates at the point, when no powdery fraction is present anymore, is higher than for lower rotation velocities. That means, the amount of small agglomerates which could bond and sinter together is higher and the contact time of the agglomerates is lower at higher velocities, i.e. decreasing the possibility of the formation of agglomerates > 2 mm. Furthermore, the higher number of collisions at higher rotation velocity affects a higher number of particle breaks²⁰. An overview of the possible agglomerate formation at lower and higher rotation velocities is shown in Fig. 5-14.

These findings are in contrast to findings by Butensky *et al.*²¹, who carried out “cold” granulation with glass spheres, finding no relationship between rotation velocity and agglomeration size distribution. This shows the limitation of these kinds of experiments, where especially sintering and clinker melt formation (as “glue” between particles) as the strengthening effects of formed agglomerates as are neglected, outlining the advantages of the RKS.

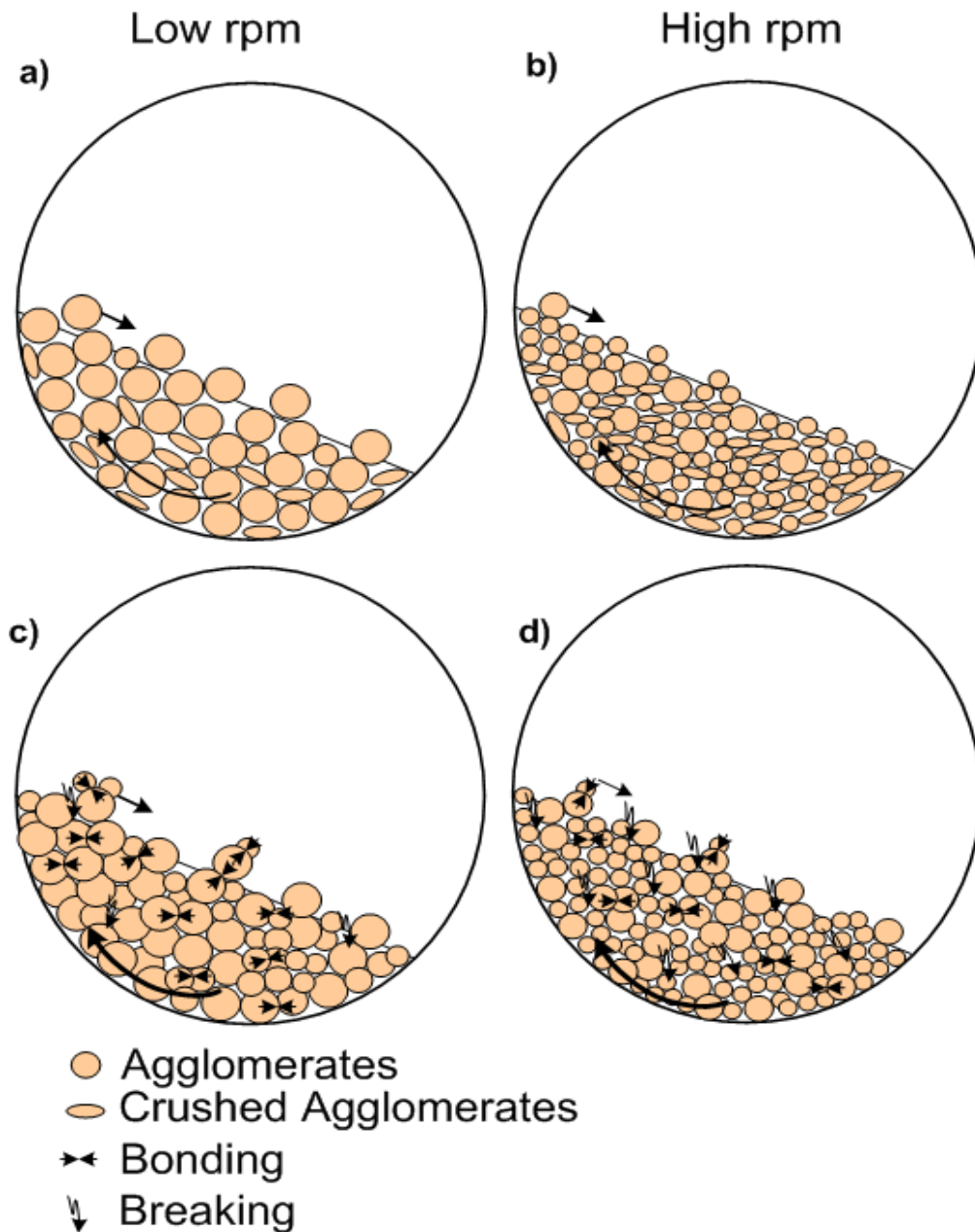


Fig 5-14: The formation of agglomerates at low and high rpm, before melt formation (a and b) and after melt formation (c and d). a) High particle contact at low rotation velocities results in bigger electrostatically formed agglomerates. b) Higher rotation, i.e. higher bed motion results in lower particle contact and higher rate of collision. Therefore, smaller agglomerates are formed in average. c) The agglomerates grow in size to sintering together with other agglomerates. The low rpm features high particle contact and less bond breakage. d) Agglomerates grow in size, too, but the average diameter of agglomerating granules is smaller, resulting together with the higher collision rate in smaller final agglomerates.

As mentioned before, the product was divided into spherical agglomerates and lining. Lining (Fig. 5-15) is bed material partly molten to the walls of the Pt/Rh material. It consisted mainly of fine agglomerates (< 0.5 mm), partly molten together, resulting in shell-like shaped lumps (Fig. 5-12h). The lining was not covering the whole surface of the inside walls of the Pt/Rh-crucible (Fig. 5-15). For all samples the amount of the spherical agglomerates and the lining was evaluated. The relative amount of the agglomerate and lining fractions are shown in Fig. 5-16 for each final temperature (Tab. C-8 - Tab. C-10 in Appendix C). Regardless of the final temperature, the relative amount of lining tends to increase with increasing rotation velocity. This is especially pronounced when increasing the rotation velocity from 5 to 15 rpm. Since the lining is mainly formed from small agglomerates (< 1 mm) this is in line with previous observations. The mineralogical and chemical composition of the agglomerates and lining obtained at 1300 °C final temperature with 5 and 15 rpm (Tab. 5-18 and Tab. 5-19) do not show any significant differences. That indicates, that no separation and enrichment of specific raw meal fractions into either lining or the agglomerates occurs, which could have resulted e.g. in the tendency of earlier melt formation of material close to the reactor walls and consequently the formation of lining. Therefore, it is assumed that the particle diameter of the agglomerates is the dominant factor on loose agglomerate or lining formation. The possibility for small particles to stick to the Pt/Rh-crucible walls is higher than for bigger agglomerates. Smaller agglomerates have a higher relative contact area with the Pt/Rh-crucible walls than bigger agglomerates, i.e. the likelihood of a layer/network of small agglomerates to stick to the wall is much higher. The stretch of contact to the wall increases, either by concentration of melt at the interface or by capturing of smaller agglomerates in the inter-agglomerate void of the layer (Fig. 5-17).

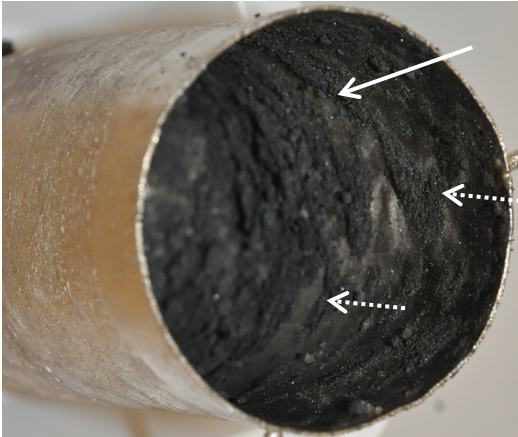


Fig. 5-15: Clinker lining on the inner wall of the Pt/Rh-crucible (solid arrow). The lining is unevenly distributed. At several spots the reactor wall is not covered by lining (dashed arrows).

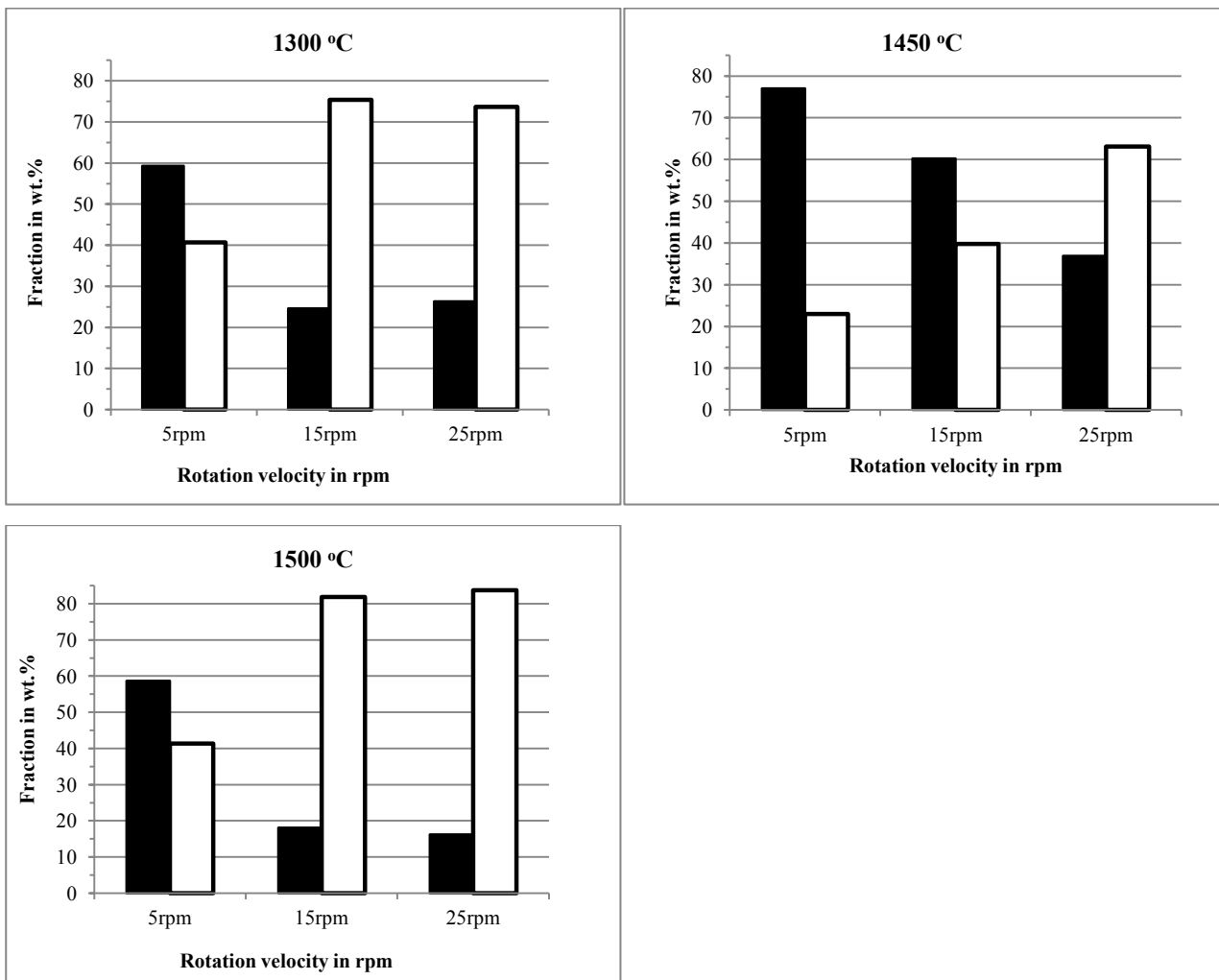


Fig. 5-16: Relative amount of agglomerates (black columns) and lining (white columns) depending on the final temperature and rotation velocity.

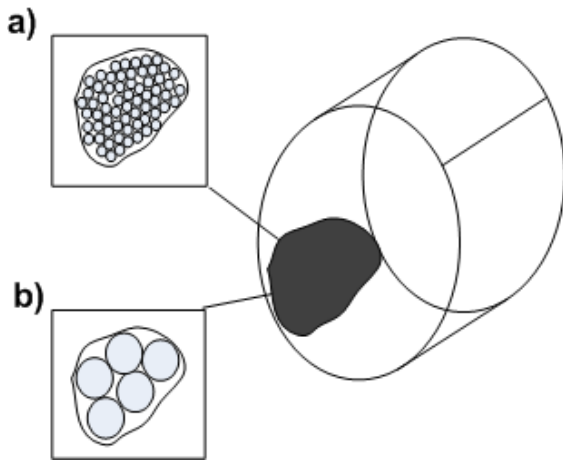


Fig. 5-17: Formation of lining. a) Smaller particles are forming a strong network, which facilitates easier sticking to the reactor walls. b) The reduced particle contact due to increased diameter of bigger agglomerates results in an easier breakage from the reactor wall, i.e. lining was not found to be formed by bigger agglomerates.

Tab. 5-18 Comparison of clinker phase composition of agglomerates and lining

	Clinker phase concentration in wt.%						
	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	MgO	CaO	Residual
5 rpm							
Agglomerates	5.4	55	5.4	4.7	0.7	20	2.5
Lining	5.4	56	4.7	2.1	0.5	23	2.7
15 rpm							
Agglomerates	3.5	54	3.9	2.6	0.7	26	1.6
Lining	4.7	59	5.9	4.1	1.0	21	-1.7

Tab. 5-19 Comparison of chemical composition of agglomerates and lining

	Chemical composition in wt.%											
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	P ₂ O ₅	K ₂ O	Na ₂ O	LSF	M _S	M _A
5 rpm												
Lining	65	22	5.4	3.1	2.0	0.3	0.2	0.6	0.2	94	2.5	1.8
15 rpm												
Agglomerates	64	21	5.4	3.1	2.0	0.3	0.2	0.6	0.2	94	2.5	1.8
Lining	65	22	5.5	3.1	2.0	0.3	0.2	0.6	0.2	94	2.6	1.8

The investigation of influence of the rotation velocity on agglomerate and lining formation in the RKS give some first ideas how an increase in the rotation velocity of the industrial rotary kiln might affect the clinker product. However, only a qualitative description and correlation for the ICRK can be derived here, since a validation of the results by means of comparison to the industrial clinker agglomerates was not carried out due to limited time.

An increase of the rotation velocity affects most likely the average agglomerate size of clinker, which becomes smaller and its relative amount higher, i.e. the size distribution might become less broad, compared to clinker obtained at lower rotation velocities. The shift towards higher relative amounts of smaller agglomerates with higher rotation velocities was shown by the agglomerate simulations in the RKS. Compared to the industrial process it is likely more pronounced, due to the higher/heavier bed material load in the industrial kiln. The shift to smaller particles sizes is caused by the crushing effect of the load of the bed material in the ICRK, which is most likely stronger at higher rotation velocities than at lower velocities. Mostly the formation of big agglomerations by cohesion and sintering of small agglomerates on bigger ones (as shown in Fig. 5-3) will be affected. The likelihood that these bonds are broken by collision with neighboring particles increases with increasing rotation velocity, since the bed material is more in motion. A correlation of the lining formation in the RKS and ICRK is somewhat more difficult to evaluate. The tendency, that smaller agglomerates are more likely to form the lining than bigger particles will also be found in the industrial kiln but of course lining formation will decrease after a layer of a certain thickness has formed under continuous operation. This shows the limits of the RKS and may suggest implementing continuous operation for a more realistic simulation.

For the validation of the results, regardless of for the lining or size distribution of agglomerates, information on industrial clinker during its formation would be necessary and requires on-site investigations with an industrial cement plant. While agglomerate size distributions can be obtained relatively easily, access to the lining is more difficult and would require access to the ICRK potentially during maintenance shut-downs. However, an established correlation between agglomerate/lining formation in the RKS and in the ICRK could aid future predictions on the influence of parameter changes, e.g. rotation rates, on the ICRK and industrial clinker utilizing the RKS.

5.5 Influence of the Heating Gradient on Clinker Formation in the RKS

As found in subsection 5.2 linear heating does not result in clinker phase composition comparable to industrial clinker, which indicated that linear heating in the RKS, i.e. a bed movement with an approximately constant rate through the kiln, might not reflect the rate in the ICRK (provided that approximations on the temperature profile within the kiln are accurate enough ²). It is reasonable to assume, that the residence time of the bed material differs in the lower and higher temperature zones in the industrial cement rotary kiln. Significant amounts of melt are formed in the range of 1350-1400°C ^{11,22,23}, making the bed material stickier and therefore slowing down the movement of the bed material. Based on this assumption heating profiles consisting of two linear gradients, i.e. simulating two bed velocities in the ICRK, are tested. The change of bed movement rate changes unlikely spontaneously in the ICRK, but gradually over the temperature range related to melt formation. Thus as a simplification, heating profiles with different switch temperatures, i.e. the temperature at which the heating rates changes, were tested. In the previous subsection the temperature range of melt formation was identified to be approximately between 1350 and 1400°C. The switch temperatures were chosen to represent the process just at the start of melt formation, when most clinker melt is formed and when the concentration of clinker melt increases only slightly (based on the details given by ²⁴), i.e. 1300 °C, 1400 °C and 1450 °C.

5.5.1 Experimental Procedure

The two different raw meals, i.e. raw meal R and raw meal Q, were used for this investigation. The samples of raw meal R were prepared as described in subsection 5.2.1 and raw meal Q samples as described in subsection 5.4.1. The heat treatment was carried out similar as described in subsection 5.1, except utilizing two heating rates (in °C/h), as described in the following.

All samples were heated within 45 min at a temperature profile from ~900-1540 °C, divided into two parts. The first part of the sample heating was from ~900 °C to one of the specified switch temperatures, and the second part from the switch temperature to 1540°C. In the test series different heating profiles were investigated by decreasing the residence time of the sample in the first part and prolonging the residence time at the second part, thus obtaining a more and more asymptotic temperature profile with respect to the maximum temperature. All heating profiles are listed in Tab. 5-20. Heating profile 1 corresponds to a linearized heating gradient, which is shown as a blue line in Fig. 5-8. Here, the heating rates (in °C/h) are equal for part one and two of the heating profile, independent of the switch temperature. In case of the switch temperature of 1300°C the heating rate in both parts was 864 °C/h, resulting in a residence time of 0.47 h between ~900-1300 °C (part 1)

and 0.28 h between 1300-1540 °C (part 2). An overview of the relevant parameters of the heating profiles is shown in Tab. 5-21. Detailed lists of the velocities are given in Tab. B-6 – Tab. B-12 in Appendix B.

Tab. 5-20 Heating profiles numbering and the corresponding residence times in the two temperature gradients.

Profile	Residence time part 1 : residence time part 2
1	Linear
2	0.5 h : 0.25 h
3	0.33 h : 0.42 h
4	0.25 h : 0.5 h
5	0.17 h : 0.58 h
6	0.08 h : 0.67 h

Tab. 5-21 List of the investigated heating profiles and corresponding heating rates depending on the used raw meal.

	Switch temperature in °C				
	Raw meal R			Raw meal Q	
Heating profile	1300	1400	1450	1400	1450
	Heating rate part 1 in °C/h : heating rate part 2 in °C/h				
1	864 : 828	-	-	-	-
2	-	-	-	1116 : 504	-
3	1260 : 540	1548 : 324	1692 : 216	-	-
4	1656 : 468	2052 : 288	2268 : 180	2088 : 281	2304 : 180
5	2484 : 396	3096 : 252	3384 : 156	-	-
6	4968 : 360	6192 : 216	6768 : 138	6264 : 209	6876 : 138

The denotation of the samples is explained on sample P3_R1300. The first letter P stands for this test series “**Profiles**”. The following number, here a 3, defines the utilized heating profile. The subscript letter identifies the used raw meal, in this case the raw meal **R**. Raw meal Q is abbreviated with Q. The last number stands for the switch temperature, i.e. 1300°C.

Furthermore, in P1_RL the last letter stands for **L**inear.

5.5.2 Results

a) Clinker Formation from Raw meal R

The average chemical composition of the three reference samples is listed in Tab. 5-22. This chemical composition is similar and therefore representative for all samples, which chemical compositions are listed in Tab. C-11 in Appendix C.

Tab. 5-22 Representative average chemical composition, LFS, M_S and M_A.

	Chemical composition in wt.%							
Sample	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	Na ₂ O	LOI
P3 _R 1400	65 ± 1	22 ± 0	5.3 ± 0.1	3.9 ± 0.0	3.0 ± 0.1	0.3 ± 0.0	0.1 ± 0.0	0.2 ± 0.1
LSF			M _S			M _A		
93 ± 1			2.4 ± 0.0			1.4 ± 0.0		

The average phase concentrations of clinker samples (from Raw meal R) obtained at different heating profiles for the switch temperature of 1300 °C are listed in Tab. 5-24, for 1400 °C in Tab. 5-25 and Tab. 5-26 and for 1450 °C in Tab. 5-27 and Tab. 5-28. The clinker phase concentrations obtained with the linear heating profile (sample P1_RL) are listed in Tab. 5-23. An overview of the development of the clinker phase concentrations is shown in Fig. 5-18.

In general, samples burned with temperature profiles 3 - 6 result in a higher alite formation, a smaller C₂S and CaO concentration than or clinker burned with the linear profile. An increase of the C₃S concentration can already be observed in the case of 1300 °C as switch temperature which qualitatively can be related to the longer residence time at temperatures >1300 °C. The average C₃S concentration of the first non-linear heated sample (P3_R1300, Tab. 5-24) increased slightly compared to P1_RL (Tab. 5-23) and the C₂S and CaO concentrations decreased accordingly. Only a small increase in clinker formation, being within the uncertainties of the XRD analysis, was observed when increasing the residence time at the higher temperatures (heating profiles 4 - 6). Free lime analysis would likely give a more precise description (cf. Tab. 5-26 and 5-28 for the other switch temperatures) but unfortunately Free lime analysis data are not available for samples P3_R1300 – P6_R1300.

The residence time above 1400 °C results in a further increase in the C_3S concentration and a decrease of the C_2S and unreacted CaO concentration (Tab. 5-25 and 5-26). Again the trends obtained from XRD analysis are not very pronounced due to the uncertainties of the method (Tab. 5-25), but the concentrations of the unreacted CaO determined by Free lime analysis show a significant decrease. Since the consumption of CaO correlates with the formation of C_3S , and therefore also with the decrease in the concentration of C_2S , the trends in concentration found by XRD analysis are supported. The higher progress in C_3S formation by non-linear heating compared to linear heating can be clearly observed by comparison of P1_{RL} (Tab. 5-23) with P3_R1400 (Tab. 5-25, 5-26). The C_3S concentration increased significantly, whereas the unreacted CaO concentration decreased. A further increase of the residence time above 1400 °C from 25 min to 40 min resulted in a significant decrease of the unreacted CaO concentration (P3_R1400 – P6_R1400 Tab. 5-23). Similar tendencies can be observed in the last test series (Tab. 5-27 and 5-27), with 1450 °C as switch temperature. Non-linear heating increases the C_3S concentration significantly (P3_R1450, Tab. 5-27), compared to linear heat treated samples (P1_{RL}, Tab. 5-23). Furthermore, the longer the residence time above the switch temperature the lower is the unreacted CaO concentration.

Tab. 5-23 Average clinker phase composition and uncertainty of clinker obtained with the linear heating profiles (switch temperature 1300°C).

		Clinker phase concentration in wt.%						
Sample	Profile	C_3S	C_2S	C_4AF	C_3A	CaO	MgO	Residual
P1 _{RL}	1	48 ± 2	27 ± 5	16 ± 2	4.3 ± 1.8	4.7 ± 1.5	1.5 ± 0.2	-0.8 ± 5.0

Tab. 5-24 Average clinker phase composition and uncertainty of clinker obtained with different heating profiles (switch temperature 1300°C).

		Clinker phase concentration in wt.%						
Sample	Profile	C_3S	C_2S	C_4AF	C_3A	CaO	MgO	Residual
P3 _R 1300	3	51 ± 0	27 ± 1	16 ± 0	3.8 ± 0.3	4.0 ± 1.3	1.5 ± 0.4	-3.8 ± 0.8
P4 _R 1300	4	51 ± 4	26 ± 1	15 ± 1	3.8 ± 0.4	5.1 ± 0.5	1.5 ± 0.2	-3.3 ± 4.5
P5 _R 1300	5	52 ± 1	24 ± 1	15 ± 0	3.6 ± 0.0	4.8 ± 1.0	1.4 ± 0.3	-0.3 ± 1.4
P6 _R 1300	6	53 ± 6	26 ± 4	15 ± 1	3.5 ± 4.0	4.3 ± 1.3	1.6 ± 0.3	-2.6 ± 5.8

Tab. 5-25 Average clinker phase composition and uncertainty of clinker obtained with different heating profiles (switch temperature 1400°C).

		Clinker phase concentration in wt.%						
Sample	Profile	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
P3 _R 1400	3	55 ± 3	23 ± 3	16 ± 2.2	4.9 ± 3.5	0.8 ± 0.1	1.2 ± 0.1	-0.9 ± 8.0
P4 _R 1400	4	57 ± 4	17 ± 3	13 ± 1.6	7.4 ± 2.8	1.0 ± 0.7	1.0 ± 0.0	3.4 ± 2.3
P5 _R 1400	5	56 ± 4	19 ± 9	14 ± 2.3	5.0 ± 3.0	0.7 ± 0.2	1.0 ± 0.9	3.9 ± 15.5
P6 _R 1400	6	57 ± 2	20 ± 7	17 ± 5.1	3.4 ± 0.0	0.8 ± 0.1	1.1 ± 0.0	1.9 ± 9.5

Tab. 5-26 Average unreacted CaO concentration and uncertainty of clinker obtained with different heating profiles (switch temperature 1400°C).

Sample	Unreacted CaO in wt.%
P3 _R 1400	2.3 ± 0.4
P4 _R 1400	1.7 ± 0.3
P5 _R 1400	1.6 ± 0.2
P6 _R 1400	1.4 ± 0.1

Tab. 5-27 Average clinker phase composition and uncertainty of clinker obtained with different heating profiles (switch temperature 1450°C).

		Clinker phase concentration in wt.%						
Sample	Profile	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
P3 _R 1450	3	57 ± 2	24 ± 8	16 ± 2	4.6 ± 2.7	0.9 ± 0.0	1.2 ± 0.1	-3.4 ± 4.4
P4 _R 1450	4	57 ± 1	23 ± 6	15 ± 3	4.8 ± 3.8	0.7 ± 0.1	1.1 ± 0.4	-0.9 ± 7.2
P5 _R 1450	5	57 ± 6	21 ± 4	14 ± 2	5.0 ± 3.2	0.8 ± 0.2	1.0 ± 0.2	1.9 ± 13.1
P6 _R 1450	6	58 ± 3	20 ± 3	14 ± 2	4.5 ± 3.0	0.6 ± 0.0	1.1 ± 0.3	1.7 ± 5.5

Tab. 5-28 Average unreacted CaO concentration and uncertainty of clinker obtained with different heating profiles (switch temperature 1450°C).

Sample	Unreacted CaO in wt.%
P3 _R 1450	1.9 ± 0.3
P4 _R 1450	1.6 ± 0.0

P5 _R 1450	1.4 ± 0.1
P6 _R 1450	1.3 ± 0.1

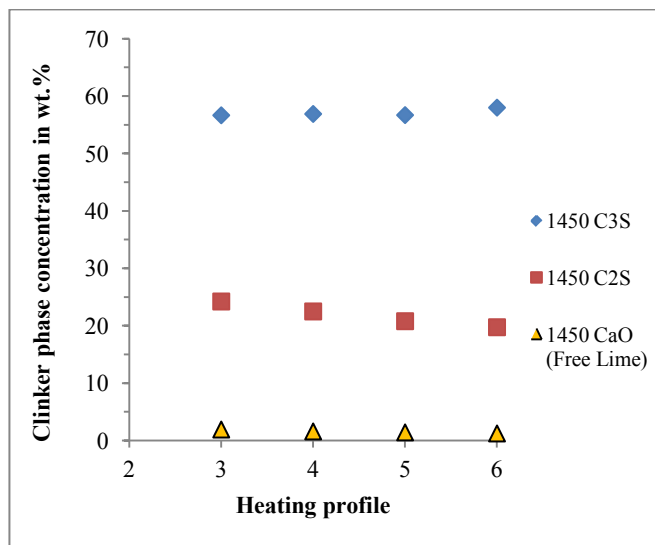
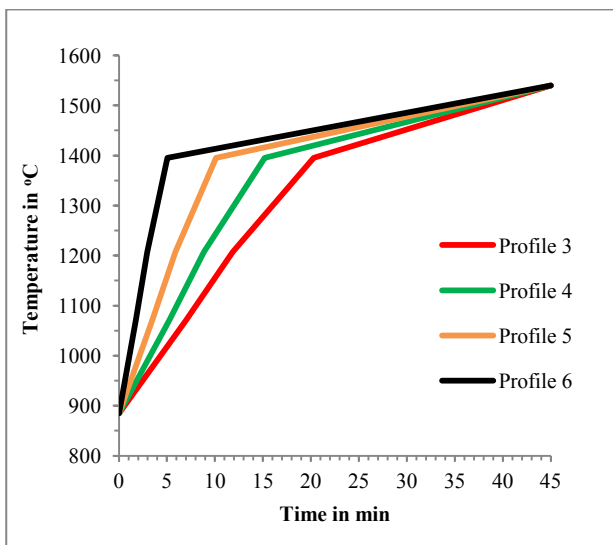
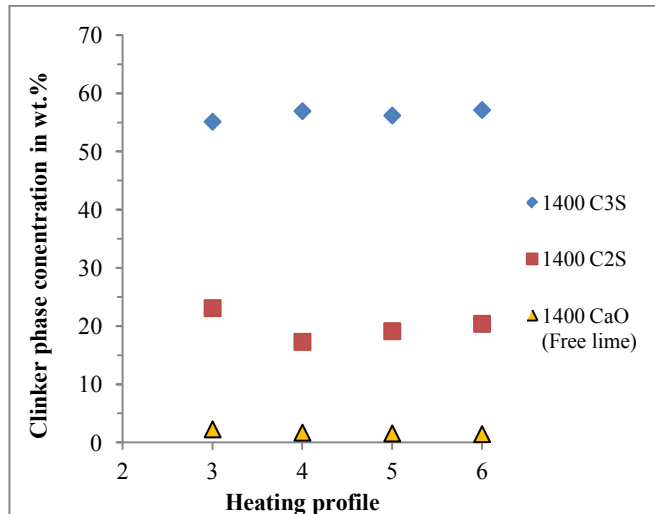
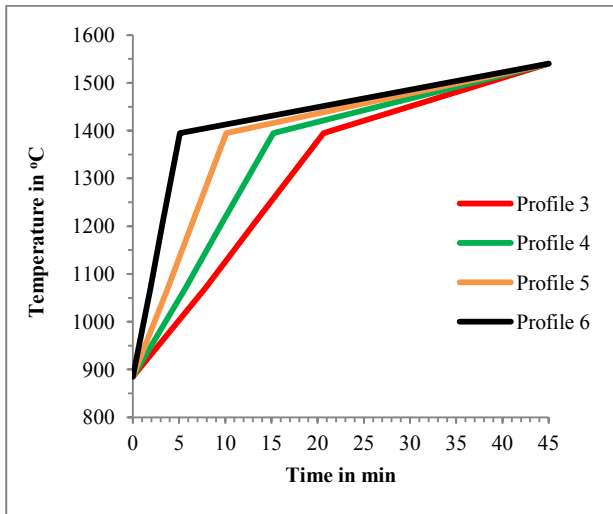
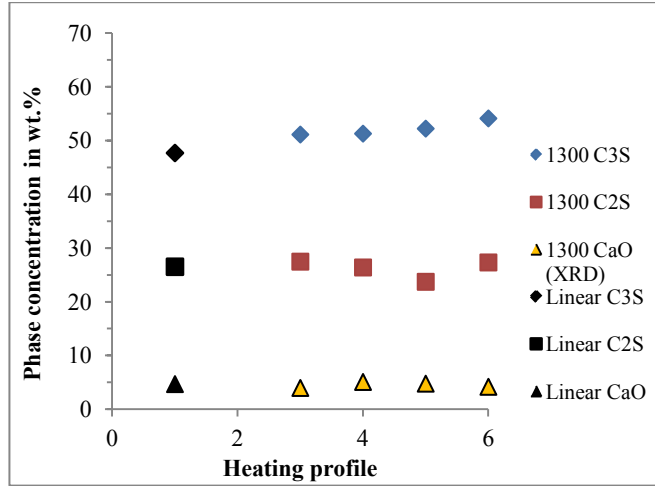
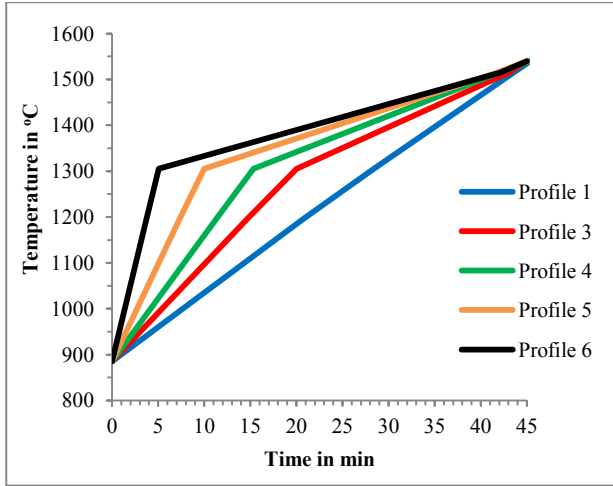


Fig. 5-18: Development of the clinker phases C_3S , C_2S and CaO dependent on the heating profile.

The particle size distribution of the sample agglomerates, heat treated using heating profiles 3 - 6 with the switch temperature $1450^{\circ}C$, are shown in Fig. 5-19 and listed in Tab C-12 in Appendix C. The dominant agglomerate size ($\sim 60 - 70$ wt.%) is >2 mm in diameter. The concentration of other size fractions decreases with decreasing agglomerate diameter. The average size of agglomerates is between 2 and 4 mm. These tendencies were observed for sample of all four profiles. Seemingly, the agglomerate formation is not depending to a high extend on the residence time at high temperatures, at least for the samples studied here.

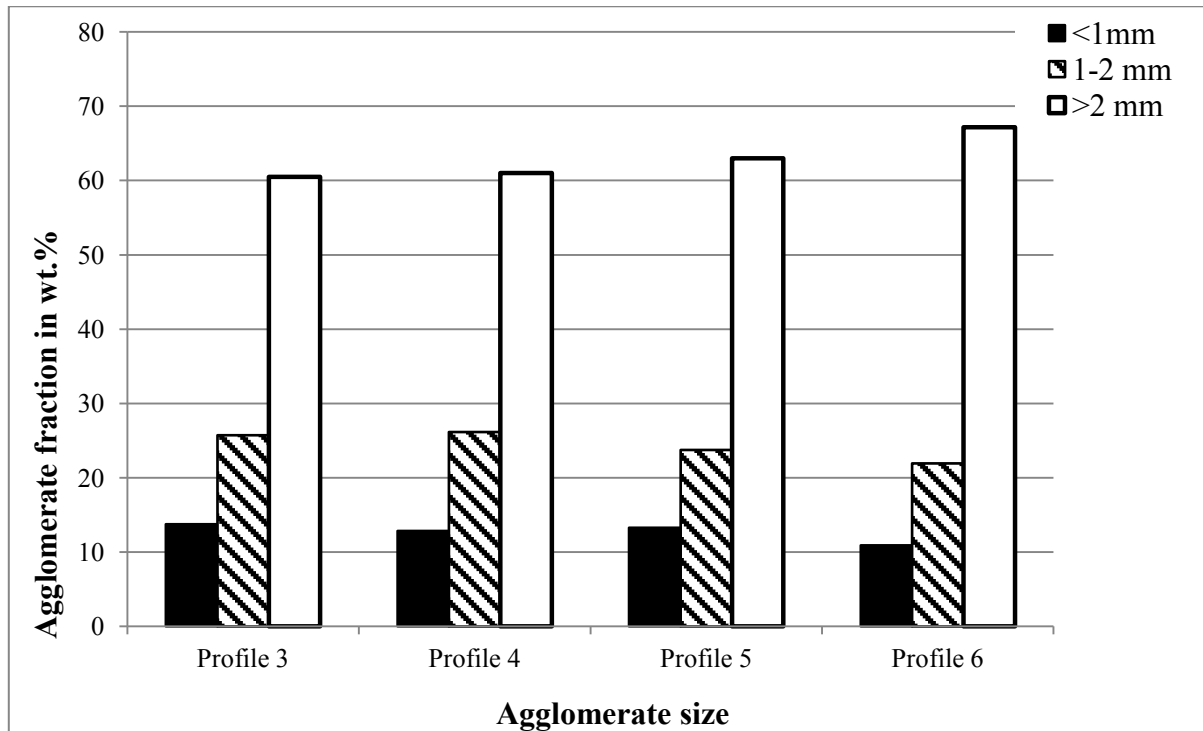


Fig. 5-19: Particle size distribution of agglomerates dependent on used heating profiles (switch temperature $1450^{\circ}C$).

In general, the non-linear heating gradients result in a higher the clinker formation, resulting in clinker phase concentrations comparable to industrial clinker (unreacted CaO concentration of ~ 1 wt.%) and therefore would be the preferable (i.e. more realistic) heating profiles for simulating the ICRK. Based on the calculation of Locher² suggesting a nearly linear temperature-location profile in the ICRK, the apparently non-linear temperature-time profiles indicate that the bed material

moves through the industrial rotary kiln with different rates, i.e. with a slower rate in the area of melt formation. With a switch temperature of 1300 °C the beneficial effect on the formation of clinker is still limited, underlining that the existence of formed melt might be important to increase alite formation significantly and furthermore that alite formation mainly occurs at temperatures significantly higher than 1300°C. But it points out, that in the ICRK the alite formation starts already to increase, when the bed velocity slows gradually down at the temperature range of melt formation.

The resulting higher residence times at high temperatures, compared to heating of bed material with constant rate, increases the degree of clinker formation, first of all due to the obvious beneficial effect of higher temperatures. Clinker formation reactions are diffusion controlled ^{25,26}; at lower temperatures mainly by CaO diffusion through solids, at higher temperatures by diffusion through clinker melt. Reaching the temperature of melt formation earlier therefore accelerates clinker formation.

A second beneficial effect is related to crystal growth. Linear heating, i.e. slow heating to temperatures below 1300/1400°C, results in the growth of belite crystals. The following reaction occurs at the interface between C₂S and diffusing CaO (see Chapter 2) forming a C₃S product layer. Further C₃S formation follows by diffusion of CaO through the new product layer towards C₂S. Regardless if the C₃S formation is considered to be a solid-liquid or a liquid state reaction ^[4,5,9,27], parts of C₂S remain a solid core surrounded by C₃S layers. The size of the core depends mostly on the size of the C₂S crystals before the alite formation starts. Full conversion of a belite core to alite emerges faster in the case of smaller particles. In non-linear heating the belite crystal grow less in size compared to linear heating profiles, since higher temperatures are reached earlier triggering the C₃S formation.

b) Clinker Formation from Raw meal Q

The effect of the previously tested temperature gradients was tested on another commercial raw meal denoted Q. Based on the previous experience it was decided, to investigate only non-linear heating profiles with switch temperatures of 1400 and 1450°C and compare those to the industrial clinker obtained from the cement plant of raw meal Q.

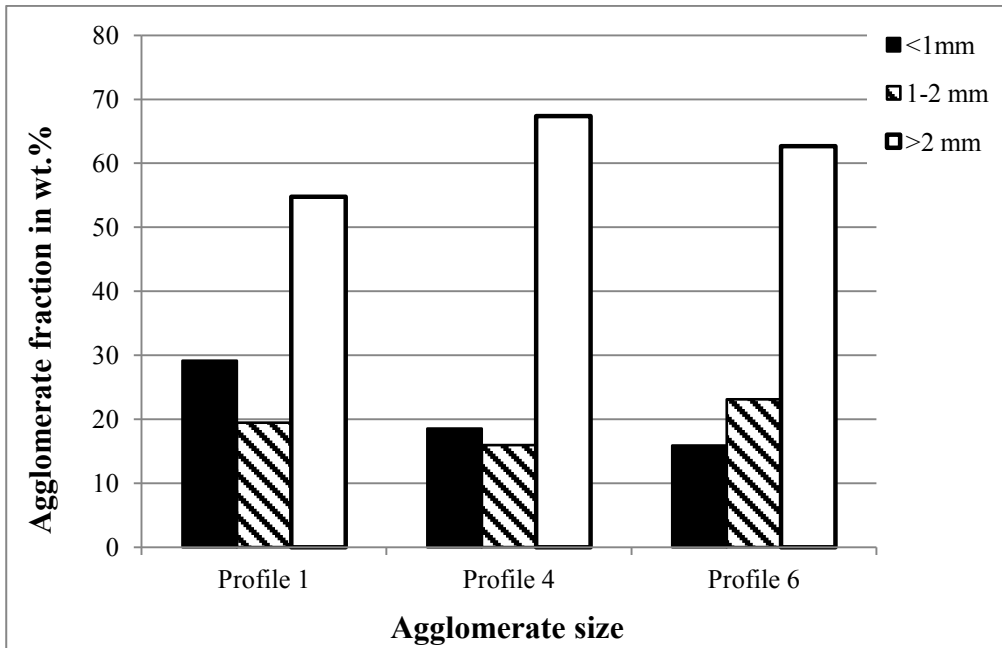


Fig. 5-20: Particle size distribution of agglomerates dependent on used heating profiles (switch temperature 1400 °C).

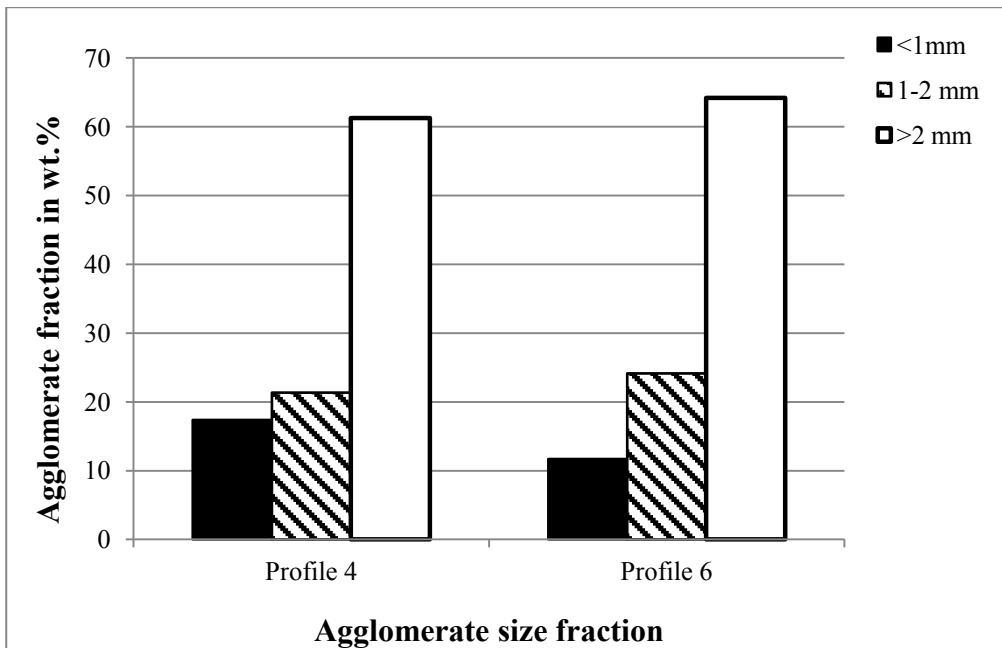


Fig. 5-21: Particle size distribution of agglomerates dependent on used heating profiles (switch temperature 1450 °C).

The size distributions of agglomerates formed under the different heat treatment conditions are shown in Fig. 5-20 and Fig. 5-21. Similar to the Raw meal R most agglomerates are larger than 2 mm, accounting for ca. 60-65 wt.% of the agglomerates. But there are also differences: increasing the residence time at higher temperature seems to affect the agglomerate formation, although the tendency is not very distinct. The amount of the smallest size fraction, <0.09-1 mm, decreases with increasing residence time. The longer residence time might aid the cohesion of smaller agglomerates and sintering of particles, resulting in the formation of stronger agglomerates which can grow in size. Since this tendency was not observed with the raw meal R before, it seems that this process is also dependent on material properties.

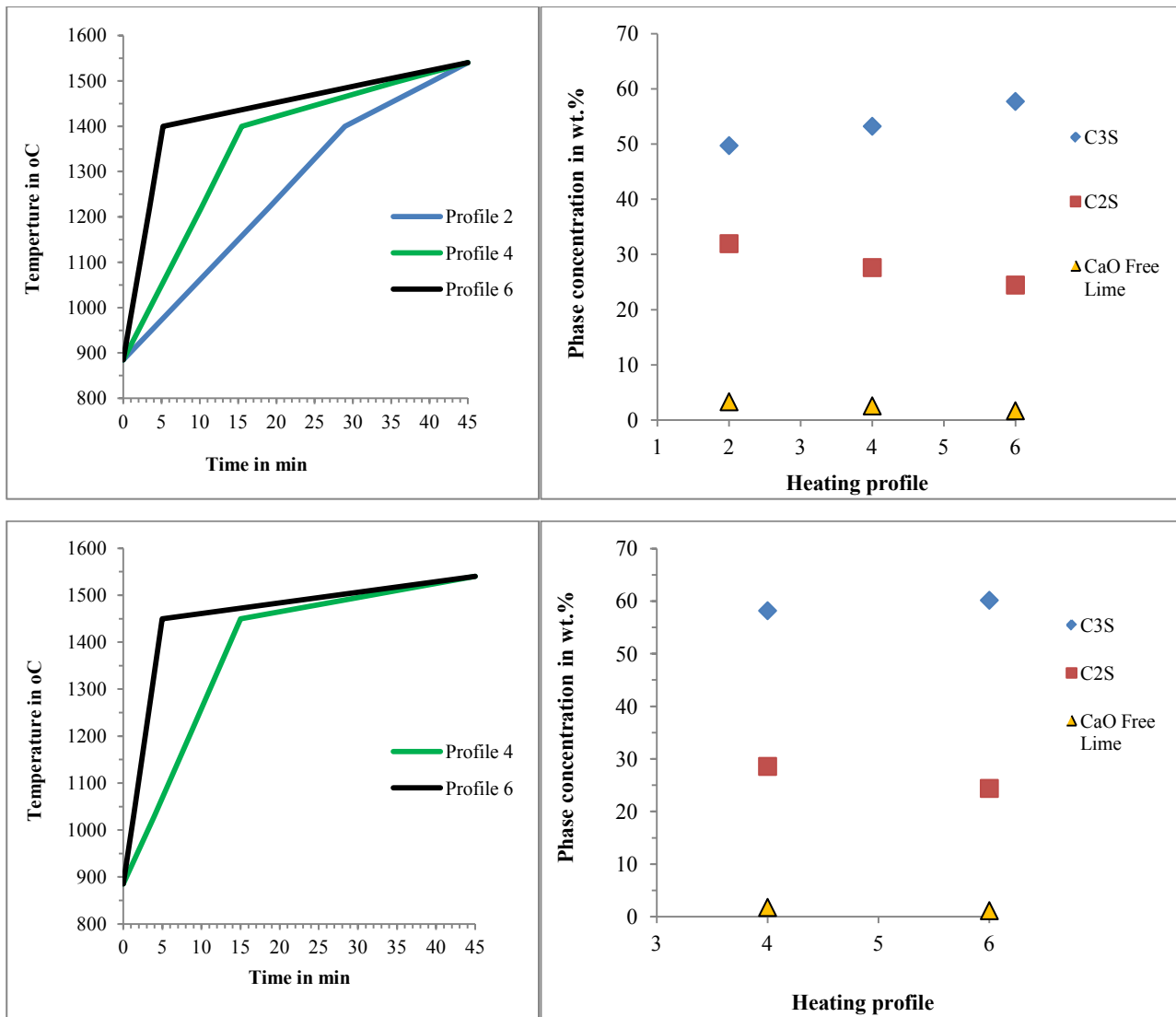


Fig. 5-22: Development of the clinker phases C_3S , C_2S and CaO dependent on the heating profile.

The phase composition of the clinker samples heat treated at different heating profiles are listed in Tab. 5-29 and 5-30 and shown in Fig. 5-22. As previously observed, the C_3S concentration increases with a higher residence time at higher temperatures. The residence time at $>1400^\circ\text{C}$ increased from P4_Q1400 to P5_Q1400 by 15 min and by 25 min to P6_Q1400, respectively, which corresponds to an increase of 10 min from P5_Q1400 to P6_Q1400. As the time increases, the unreacted CaO concentration (Tab. 5-27) decreases significantly. Similar tendencies can be found for P4_Q1450 and P6_Q1450.

The chemical composition of samples burned in the RKS (Tab. 5-31) is nearly the same as the chemical composition of the industrial clinker (Tab. 5-32), which therefore results in similar LSF , M_S and M_A . Exceptions are the concentration of K_2O and sulfur. Both concentrations are higher in the industrial clinker. In the industrial kiln the volatiles condensate at colder parts of the kiln, mainly the kiln entrance and in the preheater tower, forming deposits^{6,7}. The bed material passing those deposits thus become enriched in potassium and sulfur compounds, which is not the case in the RKS operated in batch mode. Here, volatiles are constantly removed from the reacting system by the co-current gas flow.

Note that compared to the residence time of 45 min and 30 min in the RKS, in the industrial process the residence time of the bed material is approximately 20 min²⁸. The comparison of RKS derived clinker with ICRK derived clinker shows, that similar clinker phase compositions can be achieved, although the process dominating parameter is apparently different. The most important parameters influencing the clinker phase composition are: chemical and mineralogical raw meal composition, heating rate (temperature gradient), temperature incl. maximum temperature and total residence time (see literature review Chapter 2). Since the raw meal was identical both in the RKS and ICRK the apparent difference in the necessary residence times is an indication that the maximum temperatures in the ICRK are significantly higher than the temperatures employed in the RKS and far higher than the maximum bed temperature range of $1450\text{-}1500^\circ\text{C}$ described in literature^{2,11,29,30,31}. This assumption could be further tested by burning samples for 20 min under various temperature gradients. However, this could not be done, due to the limited time of the Ph.D. project.

These data could also be used to evaluate, if the bed material could be heated effectively faster to high temperatures, since it was shown that high heating rates do apparently not affect the clinker phase and agglomerate formation negatively. Currently, the rotary kiln is the most suitable reactor

for clinkerization at temperatures $>1300\text{ }^{\circ}\text{C}$. The formation of melt, making the bed material stickier, as well as the formation of strong nodules could cause problems, if the clinkerization is carried out in a different kind of reactor, e.g. a fluidized bed reactor. However, it might be possible, to carry out the heating to $1300\text{ }^{\circ}\text{C}$ faster in a different reactor or differently designed rotary kiln.

Tab. 5-29 Average clinker phase concentration and uncertainty for different heating profiles.

Sample	Profile	Clinker phase concentration in wt. %						
		C ₃ S	C ₂ S	C ₄ AF	C ₃ A	MgO	CaO	Residual
P2 _Q 1400	2	50 ± 3	32 ± 3	15 ± 0.2	5.0 ± 2.0	0.4 ± 0.2	1.0 ± 0.6	-3 ± 1.8
P4 _Q 1400	4	53 ± 2	28 ± 1	15 ± 2.0	4.8 ± 1.8	0.4 ± 0.3	0.8 ± 0.0	-1 ± 2.1
P6 _Q 1400	6	58 ± 3	24 ± 1	14 ± 1.2	4.6 ± 3.1	0.3 ± 0.2	0.7 ± 0.1	-1 ± 1.4
P4 _Q 1450	4	58 ± 0	29 ± 3	16 ± 0.6	3.0 ± 0.3	0.6 ± 0.1	0.8 ± 0.0	-7 ± 6.6
P6 _Q 1450	6	60 ± 5	24 ± 5	15 ± 1.3	3.1 ± 1.3	0.5 ± 0.1	0.8 ± 0.2	-4 ± 9.0

Tab. 5-30 Average unreacted CaO concentration and uncertainty for different heating profiles.

Sample	Unreacted CaO in wt. %
P2 _Q 1400	3.3 ± 0.4
P4 _Q 1400	2.6 ± 0.4
P6 _Q 1400	1.7 ± 0.5
P4 _Q 1450	1.8 ± 0.1
P6 _Q 1450	1.1 ± 0.1

Tab. 5-31 Representative average chemical composition and uncertainty, LFS, M_S and M_A.

Sample	Chemical composition in wt. %									
	CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	TiO ₂	P ₂ O ₅	Na ₂ O	SO ₃	LOI
P4 _Q 1450	66±1	22±0	5.6±0.0	3.2±0.0	2.1±0.0	0.3±0.0	0.2±0.0	0.1±0.0	0.1±0.0	0.3±0.0
LSF				M _S				M _A		
94 ± 1				2.5 ± 0.1				1.7 ± 0.0		

Tab. 5-32 Industrial clinker properties of Q clinker.

Chemical composition in wt.%		Clinker phase concentration in wt.%	
CaO	66	C ₃ S	60
SiO ₂	22	C ₂ S	23
Al ₂ O ₃	5.4	C ₄ AF	11
Fe ₂ O ₃	3.0	C ₃ A	4.4
MgO	1.8	MgO	0.4
TiO ₂	0.3	CaO [‡]	0.7
P ₂ O ₅	0.1	Residual	-0.1
K ₂ O	0.6	Unreacted CaO in wt.% [*]	0.6
Na ₂ O	0.2	LSF	94
SO ₃	0.3	M _S	2.6
LOI	0.2	M _A	1.8

[‡]determined by XRD. ^{*}determined by Free lime analysis.

5.6 Summary

The commonly accepted relationship between residence times and clinker formation progress has been confirmed. However, even at a residence time significantly above the bed material residence times in the ICRK, clinker formation was less completed in the RKS. Thus, linear temperature-time heating profiles of the bed material are apparently not a realistic representation of the temperature-time profile of the material experienced in the ICRK. The stepwise formation of clinker phases with temperature in the RKS, implementing full non-isothermal heating and sample rotation, was studied and results were compared to previous studies. Similar tendencies were observed with some differences in the relevant temperature intervals. Two to three main steps in clinker formation were observed:

1. Formation of C₂S, C₃A and C₄AF (900 – 1350 °C);
2. Formation of melt phase (1350 – 1400 °C) and/or
3. C₃S formation and CaO and C₂S consumption (1350 – 1540 °C).

Agglomerates were already formed at lower temperatures (900-1000 °C) mainly due to electrostatic forces between powdery particles. The strength of these agglomerates increases with temperature as sintering and first melt formation affects the agglomerate formation. A simple kinetic model was derived and verified against the experimental data of subsection 5.2. The model allows approximate

predictions of alite and unreacted CaO concentrations for linear heat treated clinker but there is still a significant and systematic deviation which is potentially related to sintering processes occurring at lower temperatures. So far the model is applicable to raw meal composition comparable to the Raw meal R. The influence of the rotation velocity on clinker formation was investigated. The tested rotation velocities did not show any influence on the chemical and mineralogical composition of the clinker samples. However, the formation of agglomerates and of lining is affected. Increasing amounts of small agglomerates with increasing rotation velocity were found for all temperature stages (1300, 1450 and 1500 °C) of the clinker formation. This was related to the smaller contact time at higher rotation rates for the formation of strong adhesion between particles and the higher number of collisions breaking agglomerates weakly held together. Furthermore, the total amount of agglomerates decreased leading to more lining. This seems to be a result of the higher concentration of small particles, which have a higher likelihood to stick to the Pt/Rh-crucible walls. These results reflect partly the processes in the ICRK, however data from industrial plants are required to establish more reliable correlations. The effect of non-linear heating profiles on clinker formation was studied with two different industrial raw meals. The results were partly compared to industrial clinker formation conditions. It was found, that increased heating times at high temperatures increase the progress of clinker formation, resulting in phase compositions similar to industrial clinker. The results suggest that the bed material in an ICRK might not move through the kiln with constant rate, but slows down when the area of melt formation is reached. Although clinker compositions similar to industrial clinker were achieved with the RKS, the shorter residence times of bed material in the ICRK indicate higher maximum temperatures in the industrial process than suggested by the literature.

Furthermore, it was found that ~60-70 wt.% of formed agglomerates have a size of > 2mm. The formation might slightly be affected by the residence times at high temperatures, forming by trend more smaller agglomerates (< 1mm) with shorter residence times at high temperatures.

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Chapter 6

Conclusions and Future work

6.1 Conclusions

The objectives of this study have been to establish background knowledge on correlations of process conditions with respect to the development of clinker properties in a cement rotary kiln.

In an extensive literature review on clinker crystal phase formation the common knowledge on clinker formation reactions under laboratory-scale conditions has been demonstrated. However, this knowledge cannot just be translated to clinkerization processes in the industrial cement rotary kiln (ICRK), due to its complexity involving, among others, chemical and physical reactions. These were mostly studied separately in investigations.

Understanding the formation of clinker within a rotary kiln is a crucial prerequisite in optimizing the industrial process. Therefore, laboratory studies need to mimic the industrial process more carefully, taking as an example kiln rotation into account. This was realized in this project by the development of a new setup. This setup combined two most important parameters, which enabled the simulation of the industrial reactor: non-isothermal heat treatment and simultaneous rotation. The heat treatment is carried out by moving the sample through an ordinary tube heating furnace which can be programmed to simulate different temperature-location profiles up to a maximum temperature of 1550 °C. The sample can be moved with different rates, by what different temperature-time profiles for the bed material can be simulated. Simultaneously to the horizontal movement the sample can be rotated around the horizontal axis. The setup allows a high flexibility in designing experiments; mainly to simulate different operating conditions of the industrial rotary kiln, but also other high temperature studies can be carried out.

Clinker burning test in the setup featured a good reproducibility and repeatability. However, combining non-isothermal heating and rotation condition, resulted in higher uncertainties in the clinker formation.

The aim of the Ph.D.-project has been to study the dynamical development of clinker composition and the physical shape of clinker with the new RKS and relate the results to the industrial process.

Clinker formation in the new setup showed, that linear temperature-time heating profiles of the bed material, as often assumed, are not a realistic representation of the industrial process. However, non-linear temperature-time profiles, i.e. fast heating at lower temperatures and slow heating at higher temperatures, resulted in clinker compositions comparable to industrial clinker. A significant improvement of the clinker formation was observed, if the rate change occurred at a temperature where considerable amounts of clinker melt were formed (1400 °C). It is assumed, that the clinker melt formation in the industrial rotary kiln slows down the material movement through the reactor due to its increased stickiness.

The formation of agglomerates occurred already at rather low temperatures (~900°C) mainly due to electrostatic charges between powder particles of the calcined raw meal. The agglomerates are brittle, but increase in strength due to sintering with increasing temperatures, even before the formation of significant amounts of melt is expected. The rotation velocity affected the formation of agglomerates. The amount of smaller agglomerates increased with increasing rotation velocity, which is related to the smaller contact time between particles at higher rotation and the higher number of collisions breaking weakly bond particles. Furthermore, the higher rotation velocity resulted in higher amounts of material sticking to the reactor wall (lining), whereas the total amount of agglomerates decreased.

The establishment of the RKS setup will allow more realistic clinker formation studies in the future and thus potentially an experimental lab-scale access to the understanding of important parameters in the ICRK. First investigations were made within this PhD thesis but especially the difference in scale will prove challenging. On the basis of this thesis, a number of future investigations might be interesting which will be described in the following.

6.2 Future work

The rotational motion and the possibility to vary the rotation velocity in combination with various non-isothermal heating options in the RKS allows more realistic clinker formation studies compared to the mostly utilized isothermal, non-rotating heating furnaces.

One interesting study would be related to the reduction of fuel cost of the industrial process by introducing alternative fuels such as household waste, biomass, plastics, rubber, tires, sewage

sludge, waste oil and solvents to the cement production. However, their use could have problematic effects on clinker formation. The chemical composition of alternative fuels might vary from fossil fuels containing higher amounts of alkali, sulfur, chloride, phosphate and heavy metal compounds, which could be released as volatiles during combustion or remain in the non-combustible residue. Additionally, the ash residue could contain for example calcite, sand and/or glass (among others). The clinker formation can be significantly influenced by the compounds mentioned above, affecting clinker quality. Ashes of alternative fuels can be introduced into the ICRK on both ends, by combustion within the rotary kiln burner and in the calciner burner. As a consequence, the ash could affect clinker formation both at lower and higher temperatures. Both scenarios can be studied in the RKS. In the ICRK the ashes fall into the bed material and are more or less distributed within the bed material due to the rotation. The effect of the ash on clinker formation depends strongly on the location of where the ash particles enter the bed material. Ashes being early introduced into the bed material will most likely undergo reactions with the raw meal. Ashes entering the bed material close to the lower end of the rotary kiln, might only concentrate on the surface of the bed reacting only partly with the clinker before it is cooled in the clinker cooler. This could have severe consequences for the chemical and mineralogical clinker composition, e.g. higher concentration of quartz or unreacted CaO which might not be compensable by adjusting the chemical composition of the raw meal. The distribution behavior of ash and its influence on clinker formation can be studied in the RKS depending on the specific temperature at which the ash enters the bed material. Those studies could give information on the optimal alternative fuel combustion and composition to not affect clinker formation negatively.

Another topic of interest could be dealing with the cost reductions (energy and material wear cost) of raw meal grinding. The fineness of the raw meal components is of high importance for the raw meal homogeneity, which is decisive for the clinker quality (chapter 2). The critical diameters for the calcareous and siliceous fractions of the raw meal are now given as 0.125 mm and 0.045 mm. The rotation motion of the reactor facilitates the mixing of the raw meal. Higher rotation velocities increase the mixing of the bed material, i.e. a somewhat lower raw meal homogeneity would only be needed. This could in turn mean that less fine raw material grinding is necessary. A correlation of particle size distribution, raw meal/bed material homogeneity and clinker quality/quantity could be established with the RKS.

The lining formation in ICK's is very difficult to study. Nevertheless, information of the location where lining occurs, its composition and its stability, i.e. sticking on the reactor wall (and not

collapsing into the bed material thereby changing its composition), are of high importance. The study of lining formation in the RKS is possible only to a limited extent since the absolute amount of the material is greatly different from the ICRK and since the RKS is operated in batch mode. For this purpose, the RKS should be modified in order to be additionally usable in continuous operation mode. A possible reconfiguration of the setup is given in the following (Fig. 7-1): The principle is similar to an ICRK. The material is fed into the kiln on one end and moves through the reactor by rolling and due to a small inclination of the reactor. Therefore, the whole RKS should be slightly tilted at the end of the sample motion system with a changeable angle (Fig. 7-1a). Latter should be permanently inserted in the heating furnace for the time of the experiment. The tube of the motion system should be exchanged against an Al_2O_3 tube, which can better withstand the very high temperatures, so the risk of glass formation, as with the SiC tube, is eliminated. The tube of the motion system would need to be completely moved into the heating furnace before the furnace is heated up, to prevent breakage of the Al_2O_3 tube due to thermal shock. As in investigations before, the heating furnace would be set to a temperature gradient, e.g. 900-1550 °C. The raw meal is fed into an extended gas inlet, which is already constructed to be independent of the rotation motion. Due to the inclination and the rotation of the Al_2O_3 tube of the motion system the bed material would roll through the heating furnace and can be collected at other end in e.g. a platinum bowl. The difficult part will be the protection of the bed material against reactions with the Al_2O_3 tube of the motion system for which two possibilities are conceivable. One would be to insert a Pt/Rh tube inside the Al_2O_3 tube. This would allow high control over the chemical composition of the bed material, since it could be cleaned after a finalized investigation e.g. when a study of ring formation with one raw meal is finished and another raw meal should be used. The disadvantage of using a Pt/Rh-tube is the very high cost for the noble metals. Alternatively, tailor-made deeply burned MgO bricks (much like the bricks used in ICRKs) could be used to line the inside of the Al_2O_3 tube of the motion system. These bricks could be attached to the inside of the tube using the Al_2O_3 engobe, which was used for coating the SiC tube (cf. chapter 3). Since the Al_2O_3 tube has to be rather long (needs to go through the whole heating furnace), the lining will be very time consuming and needs some effort especially in the middle zone of the tube, where the walls are difficult to reach. Furthermore, the inertness of the deeply burned MgO towards reactions with clinker raw meal or clinker needs to be tested. But if this is successful, the lining with MgO brick is a rather inexpensive possibility.

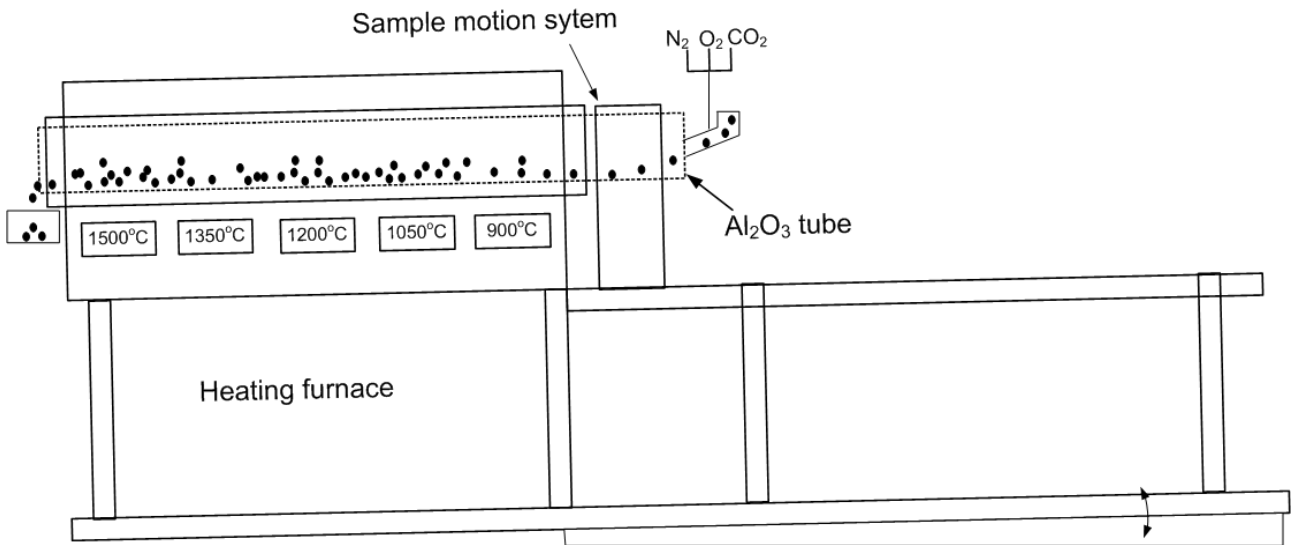


Fig. 7-1: Sketch of a possible reconstruction of the rotary kiln simulator to simulate also continuous process operation. The bed material rolls through the heating furnace inside an Al_2O_3 tube which is attached to the motions system providing sample rotations. The adjustments feature a high flexibility between batch and continuous process operations.

The results of the development of the clinker properties (chapter 6) and of further detailed investigations in the RKS could be used to develop a mathematical model, describing the different processes affecting bed particles while it is heat-treated in the RKS. This could include the motion behavior in the bed before and after formation of strong agglomerates, the chemical reactions and crystal growth. This model could provide more detailed information of bed material behavior in the industrial cement rotary kiln, since the model would be based on a more realistic clinker formation conditions as possible in ordinary clinker burning experiments.

Appendix A

Sample analysis

A.1 X-Ray Diffraction (XRD) Analysis and Rietveld Refinement

A.1.1 Theoretical Background

The XRD/Rietveld refinement method was used throughout this thesis to determine the mineralogical composition of the clinker samples. The basis of the Rietveld method is the refinement of theoretical line profiles (often peak profiles) of the crystal phases of a sample until it coincides with the measured XRD profile. The peak profile is calculated by a fundamental peak shape equation (Eq. 1), based on the assumption of Gaussian peak shape and including expressions for Lorentzian shape peak character, peak asymmetry, peak width and correction for preferred orientation. The principle of refinement of the theoretical line profile is the least square method (Eq. 2) and utilizes different functions for background and peak profile calculations.¹ In modern refinement programs, a list of those functions is available to choose from. The adequacy of the functions is evaluated by comparison of the measured and calculated XRD line profile.

$$y_i = I_k \exp \left(-4 \ln 2 \left(\frac{2\theta_i - 2\theta_k}{H_k} \right)^2 \right) \cdot (1 - P(2\theta_i - 2\theta_k)^2 \cdot \frac{s}{\tan \theta_k}) \quad (\text{Eq. 1})$$

I_k = calculated intensity of the reflection;

2θ = scattering angle;

H_k^2 = halfwidths of diffraction peak

$$M = \sum_i W(y_i(\text{obs}) - \frac{1}{c} y_i(\text{calc}))^2 \quad (\text{Eq. 2})$$

The XRD analysis measures only crystalline structures, thus amorphous phase cannot be directly quantified by the Rietveld method. However, it is possible to determine the concentration of an amorphous phase indirectly. One method is to use an internal standard of known concentration in a sample, which is analyzed. Its peak intensity in the XRD peak profile is correlated in the refinement program with the specific concentration and thus, the concentration of other crystal phases contained in the sample are calculated by comparison of the related peak intensities with the peak

intensity of the internal standard. The amorphous phase is determined as the difference between the relative amounts of the crystalline phases to 100 % (Eq. 3).

$$100 \text{ wt. \%} = \text{wt. \%}_{\text{internal standard}} + \text{wt. \%}_{\text{crystal phase}} + \text{wt. \%}_{\text{amorphous phase}} \quad (\text{Eq. 3})$$

Clinker is mainly a multi-crystalline product, but could also consist of smaller amounts of amorphous phase. If the product is quickly cooled to room temperature (which is necessary to stabilize the alite phase), the melt phase “freezes” instead of allowing C_3A and C_4AF to re-crystallize. Thus, the internal standard method was used to determine a possible amorphous phase in clinker samples. According to Westphal *et al.*² the concentration of the internal standard in a sample influences significantly the accuracy of the determination of the amorphous phase. The uncertainty of the amorphous phase quantification increases with decreasing internal standard concentrations in the analyzed samples².

A.1.2 Experimental

The basis of the XRD analysis procedure is already used by FLSmidth; some modifications were carried out: the concentration of the internal standard and the background function in the refinement settings of the utilized software (X’Pert HighScorePlus) were changed.

The internal standard concentration should be between 10 and 50 wt.% of the clinker sample². Thus, three internal standard concentrations were tested: 10, 30 and 50 wt.%. Anatase (TiO_2) was chosen as internal standard. As clinker test sample a clinker NIST standard (number 2686a) was used. The phase composition of this clinker standard is certified by the National Institute of Standards & Technology. Note that the NIST clinker does not contain an amorphous phase. The clinker phase composition is listed in Table A-1 as referenced by the National Institute of Standards & Technology³. The clinker standard was received as granulated material, which was ground for 0.5 min in a Herzog-mill. The NIST clinker was divided into three samples and internal standard was added according to Table A-2.

Appendix A: Sample analysis

Table A-1 The composition of the NIST standards.

Sample	Clinker phase concentration in wt. %					
	C ₃ S	C ₂ S	C ₃ A	C ₄ AF	MgO	Alkali sulfate
NIST 2686a	63.53	18.8	2.46	10.80	3.40	0.86
Stand. Deviation	1.04	1.10	0.39	0.84	0.23	0.17

Tab. A-2 The amount of internal standard added to the NIST clinker standards.

Sample name	sample (g)	TiO ₂ (g)	TiO ₂ wt.-%
Nist 10	1.80	0.20	10.00
Nist 30	1.40	0.60	30.00
Nist 50	1.00	1.00	50.00

These three mixtures were then wet-ground with 5 ml acetone in the Herzog-mill for 15 minutes. After grinding, the samples were dried at 80 °C for ca. 15 minutes. The samples were pressed into tablets. Here, ca. 1 g of the powder mixture was pressed into a steel ring (Fig. A-1; 1.). A disc was placed over the side of the steel ring/sample tablet which has been in touch with the pressing device (2.). The sample surface of the opposite side is used for the XRD measurement (3.). The pressed sample tablets were placed in the analysis instrument and analyzed. Only two samples at a time were placed in the analysis instrument to prevent cracking of the powder tablet due to water uptake during the measurement. The key data of the instrument settings are listed in Tab. A-3. The obtained XRD pattern of each sample was treated with software to qualify and quantify the different clinker phases in the sample.

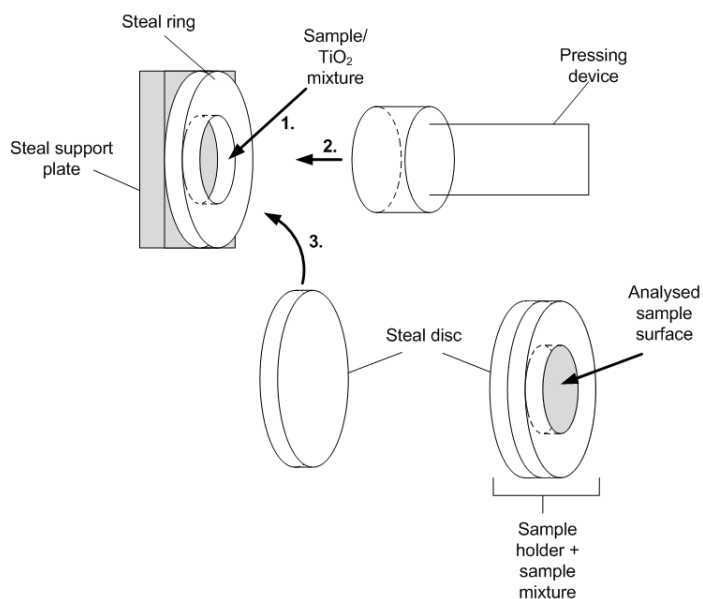


Fig. A-1: Backload method. A steel ring is attached on a steel support plate. The material is inserted into the opening of the ring and pressed to a tablet (1.). The ring is closed with a steel disc. The whole sample holder (ring + disc) is removed from the steel support plate (2.). The open side of the sample, previously covered by the steel plate is subjected to XRD analysis (3.).

Tab. A-3 Line profile measurement settings.

Instrument	XPert MPD (Panalytical)
X-ray source	Cu-cathode
K-Alpha 1	1.54006 Å
K-Alpha 2	1.54443 Å
K-Beta	1.39225 Å
K-Alpha 1/K-Alpha 2 ratio	0.5
Divergence slit size	0.25°
Specimen length	10.00 mm
Spinning	Yes
Start position	5.0° (2θ)
End position	65.0° (2θ)
Step size	0.02° (2θ)
Scan step time	300 s
Data treatment software	X'Pert HighScorePlus (Panalytical)

The quantification of the different clinker phases was carried out utilizing the Rietveld method in the X'Pert HighScorePlus program. Tab. A-4 lists the program settings and refined parameters. Additional to the listed the unit cell parameter (a , b , c , α , β , γ), the scale factor, preferred orientation and the parameters accounting for Gaussian peak characteristics were refined where applicable. The different clinker crystal phase line profiles were set already by FLSmidth laboratories.

Tab. A-4 Program settings and refined parameters in X'Pert HighScorePlus.

Settings for:	Specifics	Refined Parameters
		Program settings 2
Global Parameters	Background	Chebyshev II
		Coefficient 1-6, 23
	Profile function	Pseudo Voigt
	Max. number of least-squares cycles	20
	Least-squares type	Newton-Raphson
C_3S ⁴	Preferred orientation*	1.00 0.00 -1.00
	Unit cell	a , b , c [Å] β [°]
β - C_2S ⁵	Unit cell	a , b , c [Å] β [°]
C_4AF	Unit cell	a , b , c [Å]
	Preferred orientation*	0.00 0.00 1.00

Appendix A: Sample analysis

C ₃ A (cubic)	Unit cell	a [Å]
C ₃ A (orthorhombic)		a, c [Å]
CaO	Unit cell	a, b, c [Å]
MgO	Unit cell	a, c [Å] $\alpha, \gamma [^\circ]$
TiO ₂ (anatase)	Unit cell	a, c [Å]

* Preferred orientation accounts for a specific orientation of a crystallite phase in a specific direction (e.g. flat-plate shaped crystals) which would cause incorrect intensity measurements in multi-crystal samples ⁶.

A.1.4 Results

The line profile of NIST 30 is shown in Fig. A-2. The red pattern is the measured peak profile, the green curve the fitted background and the blue pattern is the refined peak profile. As it can be seen, the refined profile matches the measured profile well. This result was also observed for NIST 10 and NIST 50. Thus, the chosen program settings with the exchanged background function fit well.

The concentrations of the clinker phases of the NIST 10 – NIST 50 clinker obtained by the Rietveld refinement and the corrected certified phase concentrations (without alkali sulfate) are listed in Tab. A-5. The TiO₂ concentration of NIST 10 – NIST 50 samples was not fixed to the added concentration, i.e. the Rietveld refinement was used to quantify also the concentration of the internal standard which of course prevents the determination of amorphous phase. Thus, the comparison of the internal standard concentration added and the concentration calculated enables an additional qualitative estimation of the goodness of the sample refinement. The refinement results of all three NIST samples show nearly similar clinker phase concentrations as the NIST standard sample. Only minor deviations occur, which are within the uncertainty of max. ± 1.1 wt.% ³. Also, the TiO₂ concentration calculated fits in case of NIST 10 and NIST 30 the actually added TiO₂ amount and in case of NIST 50 it deviates by 2 wt.%. Thus, the refinement of all NIST clinker resulted in satisfactory determination of the clinker phase concentration. However, Westphal *et al.* ² emphasized the importance of internal standard concentrations >10 wt.% for samples with amorphous phase concentrations <10 wt.%. On the basis of these results, it was decided to use 30 wt.% of standard for future investigations.

Appendix A: Sample analysis

Tab. A-5 Comparison of the refinement of different samples of NIST clinker with NIST standard, varying in the concentration of the internal standard anatase.

Sample	Clinker phase concentration in wt. %						TiO ₂
	C ₃ S	C ₂ S	C ₃ A (ortho)	C ₃ A (cubic)	C ₄ AF	MgO	
NIST* _{certified}	64.08	18.96	2.48		10.89	3.43	-
NIST 50	65	19	0.8	2.2	9.5	4.0	52
NIST 30	64	18	1.2	2.1	10	4.5	30
NIST 10	66	18	1.3	2.2	9.6	3.3	10

* without alkali sulfates

General remarks:

After using this method successfully for some time, problems with the high positive as well negative concentrations of the amorphous phase occurred, although the preparation procedure was not changed. The cause of that cannot be explained. It was evaluated, whether the XRD analysis should be employed without using an internal standard. However, for comparison reasons it was decided to continue using an internal standard. The amorphous phase is in the following chapters denoted as residual and is used as indicator for the uncertainty of the XRD analysis. To verify XRD results, Free lime analysis was carried out to compare the concentrations of unreacted CaO.

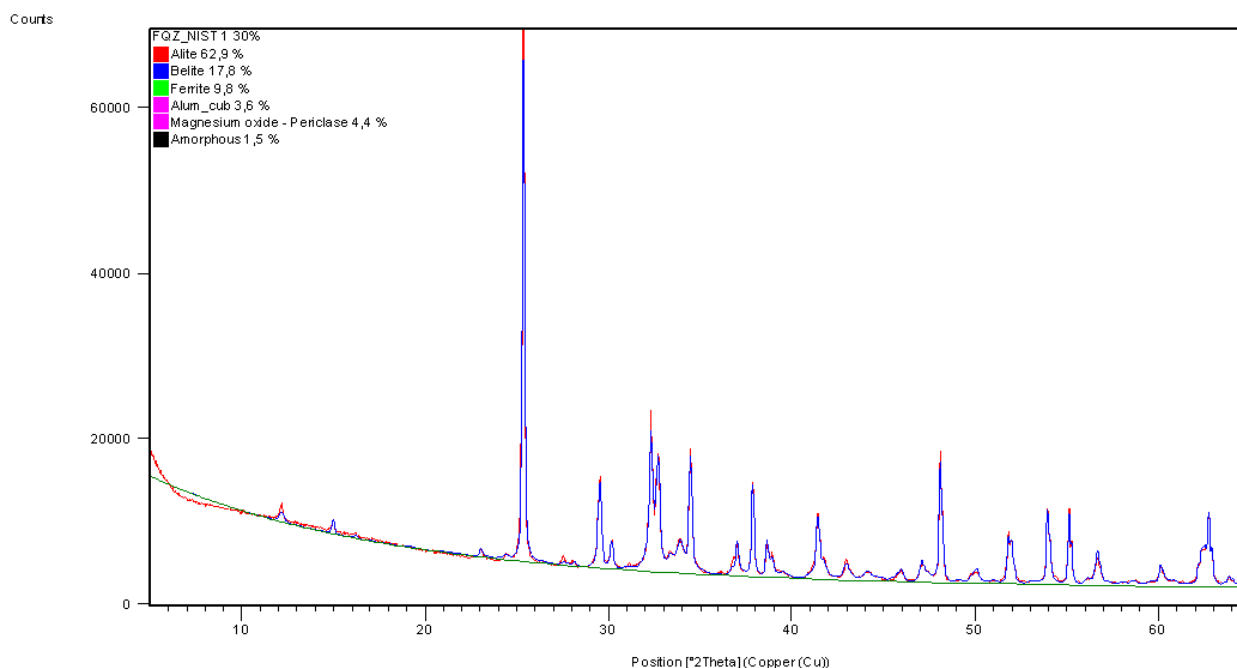


Fig. A-2: The refined line profile of NIST 30. The red pattern is the original measured profile, the blue pattern corresponds to the refined profile and the green curve is the calculated background. The refined profile fits the measured profile well, i.e. the refinement settings are satisfactory.

A.2 Other sample analysis techniques

Some of the analysis methods (XRF, Free lime analysis) are standard routines developed in the laboratories of FLSmidth. Therefore, no detailed descriptions can be given, since those methods are confidential.

A.2.1 X-ray fluorescence analysis (XRF)

The XRF analysis determines the chemical composition of the non-volatile fractions of a sample. Powder clinker samples are molten at 950 °C with a flux into a glass tablet followed by analysis in an X-Ray fluorescence spectrometer. The method was used to analyze the non-volatile chemical composition of raw meal samples of each test series batch as well as the resulting clinker samples.

A.2.2 Free Lime analysis

The Free lime analysis is a standard method in the cement field and therefore a standard routine at FLSmidth laboratories. It is based on the extraction of unreacted CaO from a powdery clinker sample by ethylene glycol and the subsequent titration of the extract with HCl. The final concentration is obtained by comparison with concentrations of a calibration curve.

The Free lime analysis is characterized by a high accuracy (0.1 % uncertainty) and is therefore a strong tool to support concentration trends observed by XRD. Although the method only determines the unreacted CaO concentration, it is also indirectly a measure for the alite concentration, since CaO is consumed for the formation of the alite at high reaction temperatures.

A.3 Reference

- (1) Rietveld HM. A profile refinement method for nuclear and magnetic structures. *J. Appl. Cryst.* **1969**, 2, 65.
- (2) Westphal T, Fuellmann T, Poellmann H. Rietveld quantification of amorphous portions with an internal standard-Mathematical consequences of the experimental approach. *Powder Diffraction* **2009**, 24, 239.
- (3) National Institute of Standards & Technology; Certificate of Analysis; Standard Reference Material ® 2686a Portland Cement Clinker. Gaithersburg 04.08.**2009**
- (4) Nishi F.; Takeuchi F. Tricalcium Silicate $\text{Ca}_3\text{O}[\text{SiO}_4]$: The monoclinic superstructure. *Zeitschrift fuer Kristallographie* **1985**, 172, 297.
- (5) Mumme WG.; Hill RJ. Bushnell-Wye G. Segnit ER. Rietveld crystal structure refinements, crystal chemistry and calculated powder diffraction data for the polymorphs of dicalcium silicate and related phases. *N.Jb. Miner. Abh.* **1995**, 169, 35.
- (6) McCusker LB. Von Dreele RB. Cox DE. Louer D. Scardi P. Rietveld refinement guidelines. *J. Appl. Cryst.* **1999**, 32, 36.

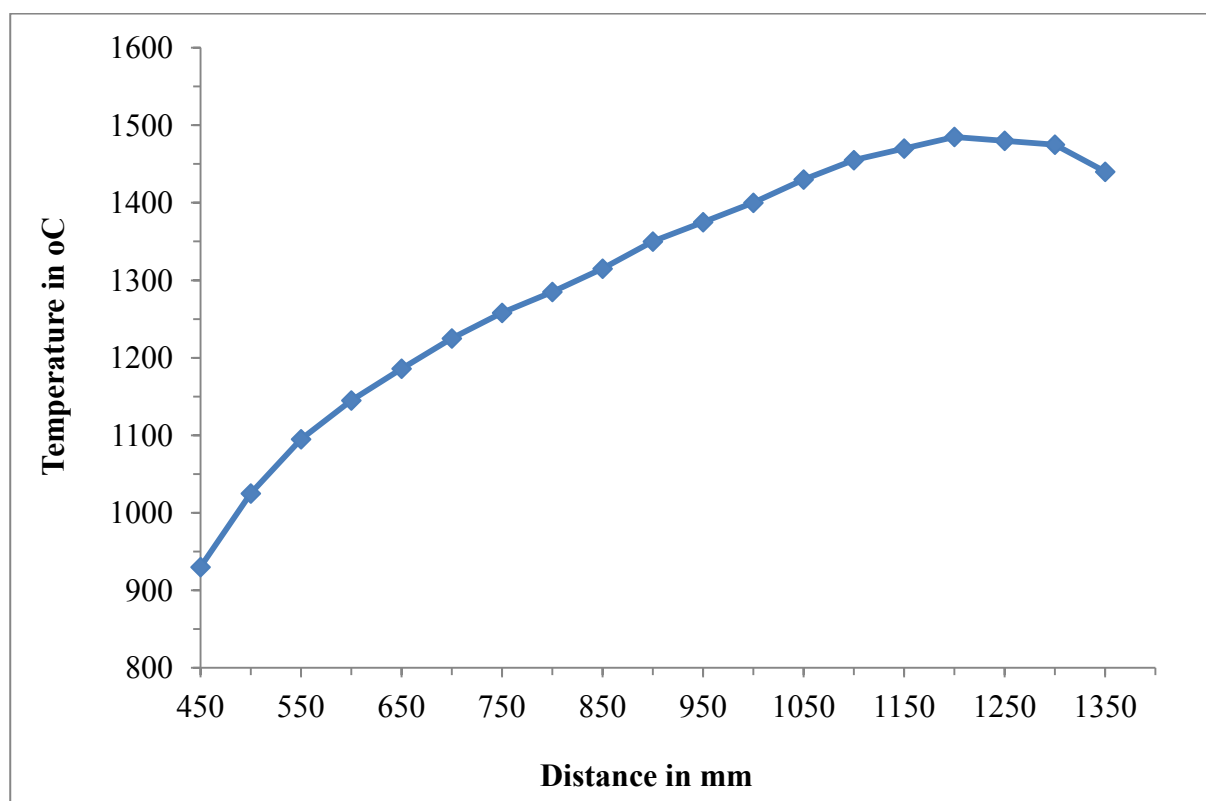
Appendix B

Temperature Profile and Sample Motion Programs

B.1 Temperature profiles

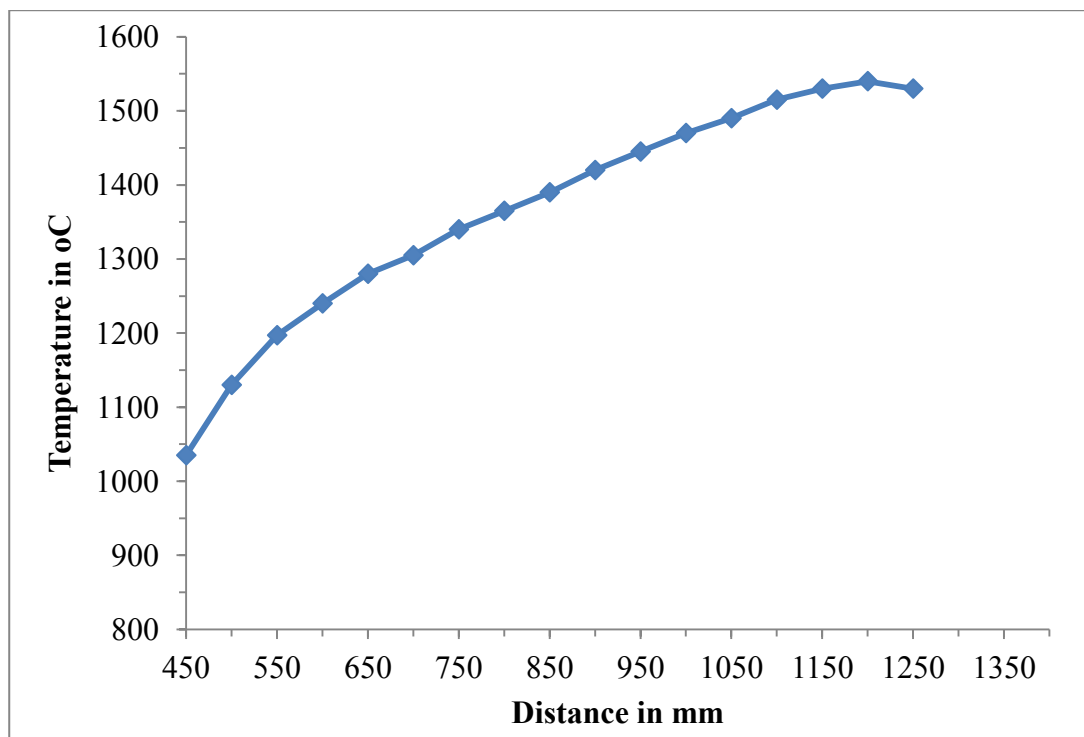
B.1.1 Profile 1

	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C:	1100	1213	1325	1438	1550



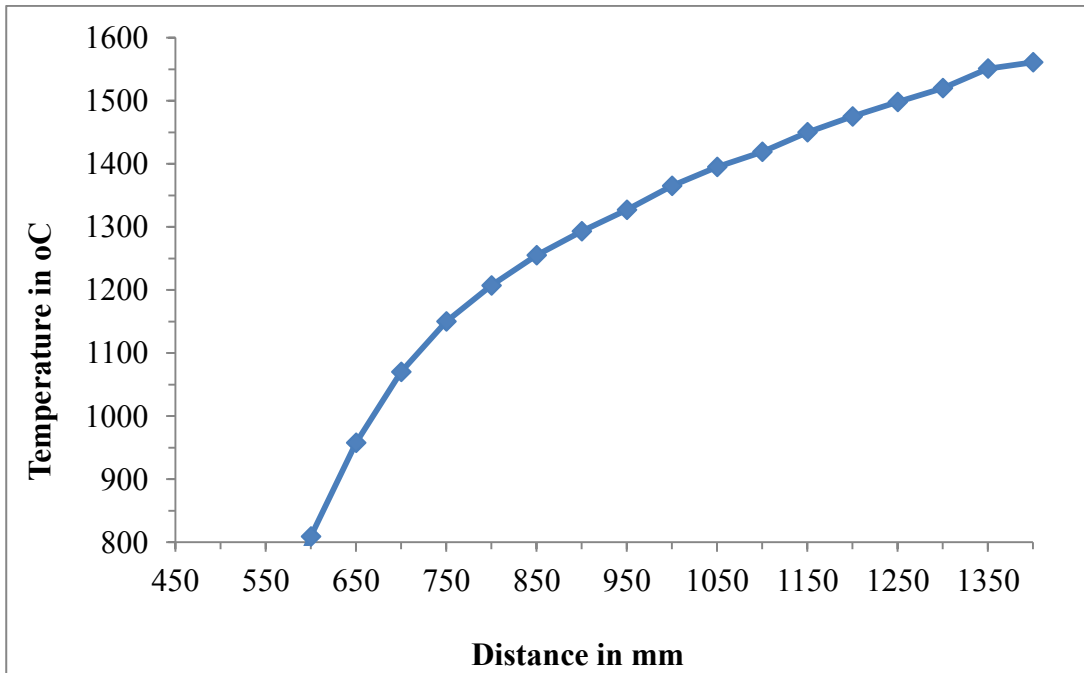
B.1.2 Profile 2

	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C:	1200	1300	1400	1500	1600



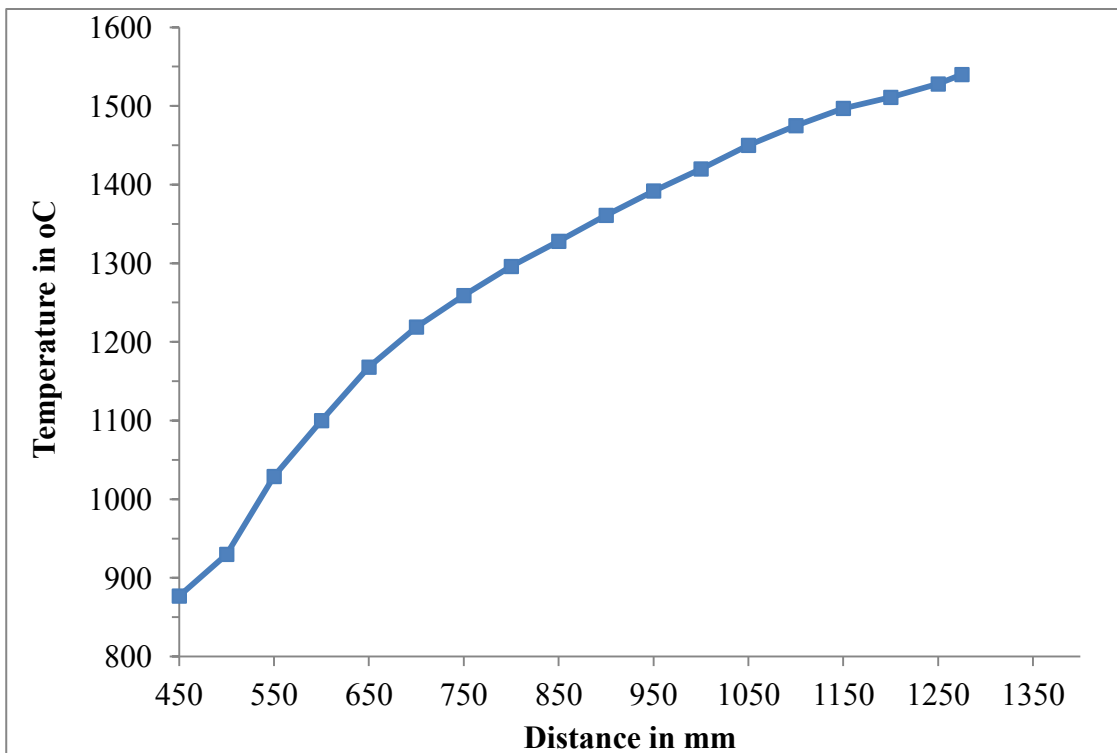
B.1.3 Profile 3

	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C:	1200	1300	1400	1500	1600



B.1.4 Profile 4

	HZ 1	HZ 2	HZ 3	HZ 4	HZ 5
Temperature in °C:	1200	1300	1400	1500	1600



B.2 Motion system programs

B.2.1 Program 1

This program was used for the repeatability studies using raw meal R, described in chapter 4.2.

Tab. B-1 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile			1		
Total distance mm			670		
ΔT in °C			585		
Section	Distance in mm	Temperature in °C	Distance per section in mm	ΔT in °C	Heating rate in °C/mm
Section 1	0-430	25-885	430	860	2.15
Section 2	430-500	885-1025	70	140	2.06
Section 3	500-750	1025-1258	250	233	0.73
Section 4	750-1050	1258-1430	300	172	0.52
Section 5	1050-1100	1430-1450	50	20	0.25

Tab. B-2 The related velocities for each section.

Max. heating time	30 min
Section	Velocity in mm/h
Section1	15
Section 2	520
Section 3	1286
Section 4	2017
Section 5	3250
Average velocity in mm/s	1512
Average heating rate in °C/h	1296

B.2.2 Program 2 and 3

Tab. B-3 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile			2		
Total distance mm			800		
ΔT in °C			655		
Section	Distance in mm	Temperature in °C	Distance per section in mm	ΔT in °C	Heating rate in °C/mm
Section 1	0-400	25-885	400	860	2.15
Section 2	440-550	885-1197	150	312	2.06
Section 3	550-700	1197-1305	150	108	0.73
Section 4	700-1100	1305-1515	400	210	0.52
Section 5	1100-1200	1515-1540	100	25	0.25

Program 2

This program was used for the repeatability studies (chapter 4.2), investigations on the heating time influence (chapter 5.2) and the temperature stepwise heating experiments (chapter 5.3).

Tab. B-4 The related velocities for each section.

Max. heating time	30 min	45 min	60 min	75 min	120 min
Section	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000	54000	54000	54000
Section 2	612	432	324	252	144
Section 3	1764	1188	900	720	432
Section 4	2484	1656	1224	1008	612
Section 5	5148	3456	2592	2052	1296
Average velocity in mm/h	1584	1080	792	648	396
Average heating rate in °C/h	1296	864	648	504	324

Program 3

This program was used for the investigations of non-linear heating profiles using raw meal R (switch temperature 1300 °C) described in chapter 5.5.

Tab. B-5 The related velocities for each section.

Heating profile	Profile 1	Profile 3	Profile 4	Profile 5	Profile 6
-----------------	-----------	-----------	-----------	-----------	-----------

Section	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000	54000	54000	54000
Section 2	426	604	806	1209	2417
Section 3	1201	1705	2274	3411	6822
Section 4	1599	1062	885	758	663
Section 5	3325	2208	1840	1577	1380

B.2.3 Program 4

This program was used for the investigations of non-linear heating profiles using raw meal R (switch temperature 1400 °C) described in chapter 5.5.

Tab. B-6 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile			3		
Total distance mm			691		
ΔT in °C			655		
Section	Distance in mm	Temperature in °C	Distance per section in mm	ΔT in °C	Heating rate in °C/mm
Section 1	0-625	25-885	625	860	2.15
Section 2	625-700	885-1070	75	185	2.61
Section 3	700-800	1070-1207	100	137	1.37
Section 4	800-1050	1207-1395	250	188	0.76
Section 5	1050-1320	1395-1540	270	145	0.52

Tab. B-6 The related velocities for each section.

Max. heating time	Profile 3	Profile 4	Profile 5	Profile 6
Section	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000	54000	54000
Section 2	592	789	1184	2368
Section 3	1128	1504	2255	4511
Section 4	2033	2711	4066	8132
Section 5	646	538	462	404

B.2.4 Program 5

This program was used for the investigations of non-linear heating profiles using raw meal R (switch temperature 1450 °C) described in chapter 5.5.

Tab. B-7 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile			3		
Total distance mm			691		
ΔT in °C			655		
Section	Distance in mm	Temperature in °C	Distance per section in mm	ΔT in °C	Heating rate in °C/mm
Section 1	0-625	25-885	625	860	2.15
Section 2	625-700	885-1070	75	185	2.61
Section 3	700-800	1070-1207	100	137	1.37
Section 4	800-1150	1207-1450	350	243	0.76
Section 5	1150-1320	1450-1540	170	90	0.52

Tab. B-8 The related velocities for each section.

Max. heating time	Profile 3	Profile 4	Profile 5	Profile 6
Section	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000	54000	54000
Section 2	649	866	1299	2598
Section 3	1237	1650	2474	4949
Section 4	2493	3324	4985	9971
Section 5	432	360	309	270

B.2.5 Program 6

This program was used for the investigations of non-linear heating profiles using raw meal Q (switch temperature 1400 °C) described in chapter 5.5.

Tab. B-9 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile		4
Total distance mm		825

ΔT in $^{\circ}\text{C}$			655		
Section	Distance in mm	Temperature in $^{\circ}\text{C}$	Distance per section in mm	ΔT in $^{\circ}\text{C}$	Heating rate in $^{\circ}\text{C}/\text{mm}$
Section 1	0-450	25-885	450	860	2.15
Section 2	450-700	885-1219	250	334	1.4
Section 3	700-970	1219-1400	270	181	0.7
Section 4	970-1150	1400-1497	180	97	0.5
Section 5	1150-1275	1497-1540	125	43	0.3

Tab. B-10 The related velocities for each section.

Max. heating time	Profile 2	Profile 4	Profile 6
Section	Velocity in mm/h	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000	54000
Section 2	778	1467	4402
Section 3	1613	3043	9130
Section 4	955	528	396
Section 5	1493	826	619

B.2.6 Program 7

This program was used for the investigations of non-linear heating profiles using meal Q (switch temperature 1450°C) described in chapter 5.5.

Tab. B-11 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile			4		
Total distance mm			825		
ΔT in $^{\circ}\text{C}$			655		
Section	Distance in mm	Temperature in $^{\circ}\text{C}$	Distance per section in mm	ΔT in $^{\circ}\text{C}$	Heating rate in $^{\circ}\text{C}/\text{mm}$
Section 1	0-450	25-885	450	860	2.15
Section 2	450-550	885-1029	100	144	1.4

Section 3	550-700	1029-1219	150	190	0.7
Section 4	700-1050	1219-1450	350	231	0.5
Section 5	1050-1275	1450-1540	225	90	0.3

Tab. B-12 The related velocities for each section.

Max. heating time	Profile 4	Profile 6
Section	Velocity in mm/h	Velocity in mm/h
Section1	54000	54000
Section 2	1508	4524
Section 3	1796	5389
Section 4	3510	10530
Section 5	469	352

B.2.7 Program 8

This program was used for the investigations of rotation velocity influences using raw meal Q described in chapter 5.4.

Tab. B-13 List of five sections for with the related distances, temperature increase and heating rates.

Temperature profile		4		
Total distance mm		825		
ΔT in °C		655		
Section	Temperature in °C	Velocity in mm/h	ΔT in °C	Heating rate in °C/mm
Section 1	25-885	5400	860	2.15
Section 2	885-1029	612	144	1.4
Section 3	1029-1219	1764	190	0.7
Section 4	1219-1450	2484	231	0.5
Section 5	1450-1540	5148	90	0.3

Tab. B-14 The related velocities for each section.

End temperature		1300 °C	1450 °C	1500 °C
Section	Distance in mm	Distance per section	Distance per section	Distance per section

		in mm	in mm	in mm
Section1	0-450	450	450	450
Section 2	450-550	200	200	200
Section 3	550-700	150	250	250
Section 4	700-1050		150	150
Section 5	1050-1275			120

Appendix C

Tables

Tab. C-1 List of chemicals, the producer and the purity, particle size.

Chemical	Supplier	Purity
Aluminium oxide	Sigma-Aldrich	99.7% trace metal basis
Silicon dioxide	Sigma-Aldrich	99%
Calcium carbonate	Sigma-Aldrich	Puriss. p.a. $\geq 99\%$
Iron oxide	Sigma-Aldrich	Puriss. p.a. $\geq 99.0\%$
Potassium carbonate	Sigma-Aldrich	Puriss. p.a. $\geq 99\%$
Calcium sulfate dihydrate	Sigma-Aldrich	Puriss. p.a. $\geq 99\%$
Calcium phosphate	Sigma-Aldrich	Purum. P.a. $\geq 96\%$
Sodium carbonate	Sigma-Aldrich	ACS reagent $\geq 99.5\%$
Magnesium oxide	Sigma-Aldrich	$\geq 99\%$ trace metal basis

Tab. C-2 Clinker phase composition determined by XRD. C-2

		Clinker phase concentration in wt.-%						
Sample name	Burning temperature	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	CaO	MgO	Residual
In _{Is} R 1	1400	39	31	16	5.1	3.2	1.6	4.9
In _{Is} R 2	1400	37	31	15	5.3	3.9	1.4	5.6
In _{Is} R 3	1400	39	30	15	5.3	3.3	1.3	6.3
In _{Is} R 4	1450	44	27	14	4.6	2.5	1.4	6.4
In _{Is} R 5	1450	44	27	15	4.5	3.5	1.7	4.8
In _{Is} R 6	1450	42	26	14	5.6	4.5	1.5	6.9
In _{Is} R 7	1500	55	21	15	4.7	1.2	1.9	1.5
In _{Is} R 8	1500	54	20	15	4.4	1.4	1.3	3.7
In _{Is} R 9	1500	52	21	14	4.6	0.8	1.5	5.0
In _{Is} R 10	1550	54	17	13	4.9	1.9	1.1	8.3
In _{Is} R 11	1550	53	20	13	4.5	2.1	1.3	6.0
In _{Is} R 12	1550	55	20	13	5.4	2.1	1.6	3.1

Tab. C-3 Unreacted CaO in samples determined by Free lime analysis.

Sample name	CaO in wt. %
In _{Is} R 1	5.4
In _{Is} R 2	6.0
In _{Is} R 3	5.9
In _{Is} R 4	4.0
In _{Is} R 5	n.d.*
In _{Is} R 6	5.2
In _{Is} R 7	2.6
In _{Is} R 8	2.6
In _{Is} R 9	2.6
In _{Is} R 10	1.6
In _{Is} R 11	1.7
In _{Is} R 12	1.8

* not determined.

Tab. C-4 Clinker phase composition of samples heat treated at 1300, 1450 and 1500 °C at different rotation velocities.

Sample	Clinker phase concentration in wt. %						
	C ₃ S	C ₂ S	C ₄ AF	C ₃ A	MgO	Residual	CaO
V5 _Q 1300	4.6 ± 1.2	58 ± 0	6.6 ± 0.7	3.6 ± 0.1	1.0 ± 0.2	-3.4 ± 2.1	23 ± 0.3
V15 _Q 1300	4.8 ± 6.4	60 ± 4	6.0 ± 4.5	4.1 ± 0.6	1.0 ± 0.1	-4.5 ± 0.4	22 ± 7.6
V25 _Q 1300	3.6 ± 4.0	59 ± 3	4.3 ± 0.2	3.7 ± 0.5	1.0 ± 0.2	-3.5 ± 2.8	25 ± 0.6
V5 _Q 1450	31 ± 2	49 ± 2	11 ± 2.9	6.1 ± 1.0	0.7 ± 0.2	-8.3 ± 2.6	8.2 ± 9.7
V15 _Q 1450	29 ± 0	48 ± 4	11 ± 4.5	5.9 ± 0.6	0.6 ± 0.3	-4.4 ± 0.3	7.3 ± 7.3
V25 _Q 1450	30 ± 6	47 ± 4	11 ± 4.5	5.9 ± 0.6	0.6 ± 0.1	-5.3 ± 3.9	8.3 ± 9.9
V5 _Q 1500	41 ± 5	38 ± 12	11 ± 0.8	5.2 ± 0.6	0.6 ± 0.3	-4.4 ± 10.8	7.1 ± 4.3
V15 _Q 1500	36 ± 2	44 ± 0	10 ± 0.1	5.2 ± 0.4	0.6 ± 0.6	-7.4 ± 4.4	8.8 ± 1.6
V25 _Q 1500	35 ± 7	42 ± 3	10 ± 1	5.0 ± 0	0.6 ± 0	-3.6 ± 3.9	8.2 ± 2.2

Tab. C-5 Particle size distribution of agglomerates heat treated till 1300 °C.

Fraction size	Agglomerate fraction in wt. %		
	V5 _Q 1300	V15 _Q 1300	V25 _Q 1300
>2 mm	58 ± 12	41 ± 9	41 ± 9
1-2 mm	15 ± 3	15 ± 2	14 ± 6

< 1mm	25 ± 10	44 ± 6	45 ± 8
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Tab. C-6 Particle size distribution of agglomerates heat treated till 1450 °C.

	Agglomerate fraction in wt.%		
Fraction size	V5 _Q 1450	V15 _Q 1450	V25 _Q 1450
>2 mm	67 ± 3	62 ± 17	42 ± 23
1-2 mm	18 ± 4	12 ± 2	14 ± 0
< 1mm	15 ± 4	26 ± 19	44 ± 2

Tab. C-7 Particle size distribution of agglomerates heat treated till 1500 °C.

	Agglomerate fraction in wt.%		
Fraction size	V5 _Q 1500	V15 _Q 1500	V25 _Q 1500
>2 mm	68 ± 16	44 ± 1	46 ± 51
1-2 mm	16 ± 13	18 ± 4	15 ± 4
< 1mm	16 ± 16	37 ± 5	40 ± 51

Tab. C-8 Relative agglomerate and lining content dependent on the rotation velocity (1300 °C final temperature).

	Fraction in wt.%		
	V5 _Q 1300	V15 _Q 1300	V25 _Q 1300
Agglomerates	59 ± 8	25 ± 24	26 ± 35
Lining	41 ± 8	75 ± 24	74 ± 35

Tab. C-9 Relative agglomerate and lining content dependent on the rotation velocity (1450 °C final temperature).

	Fraction in wt.%		
	V5 _Q 1450	V15 _Q 1450	V25 _Q 1450
Agglomerates	77 ± 5	60 ± 29	37 ± 3
Lining	23 ± 2	40 ± 29	63 ± 3

Tab. C-10 Relative agglomerate and lining content dependent on the rotation velocity (1500 °C final temperature).

	Fraction in wt.%		
	V5 _Q 1500	V15 _Q 1500	V25 _Q 1500
Agglomerates	59 ± 47	18 ± 24	16 ± 44
Lining	41 ± 47	82 ± 24	84 ± 44

Tab. C-11 Chemical composition of clinker from raw meal R derived at different heating profiles.

		SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	TiO ₂	Na ₂ O
Sample	Profile	22	5.4	3.9	65	3.0	0.3	0.1
P3 _R 1400	3	22	5.4	3.9	65	3.0	0.3	0.1
P4 _R 1400	4	22	5.4	3.9	65	3.0	0.3	0.1
P5 _R 1400	5	22	5.4	3.9	65	3.0	0.3	0.1
P6 _R 1400	6	22	5.3	3.9	65	3.0	0.3	0.1
P3 _R 1450	3	22	5.3	3.9	65	3.0	0.3	0.1
P4 _R 1450	4	22	5.4	3.9	65	3.0	0.3	0.1
P5 _R 1450	5	22	5.3	3.9	65	3.0	0.3	0.1
P6 _R 1450	6	22	5.4	3.9	65	3.0	0.3	0.1

Tab. C-12 Particle size distribution of the sample agglomerates heat treated at different heating profiles with the switch temperature 1450°C.

	Profile			
	3	4	5	6
>2 mm	60 ± 5	61 ± 3	63 ± 18	67 ± 8
1-2 mm	26 ± 3	26 ± 3	24 ± 8	22 ± 4
<1mm	14 ± 2	13 ± 0	13 ± 10	11 ± 4